Structures, ionic conductivity and atomic diffusion in

$A(Ti_{1-x}Fe_x)O_{3-\delta}$ - derived perovskites ($A=$Ca, Sr, Ba)

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Motivation

Production and distribution of energy affect all sectors of the global economy. The increasing industrialisation of the world requires sustainable, highly efficient energy production. Without a major technology advance, energy production will impact the quality of life on earth. For this reason, the application of the fuel cell technologies may be one of the most important technological advancement of the next decades.

The ability to draw sufficient power from a fuel cell critically depends on the rate at which ions are transported across the membrane separating the two sources of fuel. For example, the H\textsubscript{2}-O\textsubscript{2} solid oxide fuel cell (SOFC) requires rapid ion conduction across an oxide membrane (the electrolyte) [1]. High oxygen ion conductivity is also essential for a quick response to changes in oxygen partial pressures in a solid-state oxygen sensor and for an efficient oxygen separation with oxide membrane [2-3]. The material used commercially in SOFCs and sensors does not achieve a conductivity of $10^{-2}$ S/cm until 700°C; thus SOFCs and oxygen sensors are typically operated at temperatures higher then 900°C. A further development and optimization of oxide conductors suitable for use at lower temperatures require an understanding of the mechanisms by which anions move in the solid and, thus, a determination of the oxygen sites that contribute to the conductivity and those that remain trapped in the solid.

The alkaline earth titanates CaTiO\textsubscript{3}, SrTiO\textsubscript{3} and BaTiO\textsubscript{3} are ideal materials from which to base further perovskite-type compositions for numerous applications in electronics, electroceramics and sensors [4-7]. As these parent materials exhibit interesting transport properties as well as good thermodynamic stability over large ranges of temperature and oxygen partial pressure, a promising field of application is for high temperature electrochemical devices including oxygen separation membranes and SOFCs. The large number of applications of the titanates has resulted in well-developed processing technologies and a detailed understanding of the physico-chemical properties of these materials [3-7].

The aristotype CaTiO\textsubscript{3} does not contain oxygen vacancies in significant quantities and hence atomic diffusion is almost absent. Diffusion takes place because of the presence of imperfections or defects. Anion vacancies can be formed by a substitution of cations with different valence, for example the substitution of Fe\textsuperscript{3+} for Ti\textsuperscript{4+}, and both the abundance and arrangement of these anion vacancies can have a profound effect on physical properties such as electrical transport.
Point defects, that is vacancies, are responsible for oxygen lattice diffusion, which is often synonymously termed volume or bulk diffusion. In this case one can introduce the definition of the \textit{macroscopic diffusion}. The driving force is a gradient of the chemical potential. Macroscopic diffusion is characterized by a particle flux which is also called the particle density and means particle crossing a unit area per unit time. The current density divided by the electric field yields the conductivity. A direct relationship between ionic dc conductivity $\sigma$ and the diffusion coefficient $D$ is described by Nernst-Einstein equation. The fastest imaginable diffusion process would be the free flight of the particles between sites with an upper limit $D$ which is given by the expression of the diffusion coefficient of an ideal gas, $D_{\text{gas}} = \frac{\lambda \overline{v}}{3}$ where $\lambda$ and $\overline{v}$ are the mean free path and mean speed respectively. In general conductivity of the material consists of the superposition of the contribution of different types of motion, like local motion which does not involve a mass transport and deals with a single particle diffusion. Such type of motion does not contribute to the current transfer and thus not detectable by electrical conductivity.

The \textit{microscopical diffusion} process occurs in thermodynamical equilibrium and characterized by single particle diffusion. Microscopically diffusion is characterized by the following parameters:

- the jump rate $\Gamma$
- the jump vector from site 1 to site 2, $\vec{r}_{1\rightarrow2}$

If all jump rates are equal, then the residence time $\tau$ of the particle on its site is given by $\Gamma = \frac{1}{z \tau}$ where $z$ is the coordination number indicating the number of neighbouring sites. If the jump vectors have the same length it make sense to introduce the jump length $l = |\vec{r}_{1\rightarrow2}|$; otherwise $l$ represents an average jump length.

The central connection between microscopical and microscopical diffusion is the Einstein-Smoluchowski relation:

$$D = \frac{l^2}{2 \cdot d \cdot \tau},$$

where $D$ is diffusion coefficient and $d = \{1, 2, 3\}$ the dimensionality of the diffusive process. This equation considers only the simple case that all sites are energetically equivalent and only diffusion jumps to the neighbour sites are allowed.

There are numerous experimental methods for studying diffusion in solids (Table 1). The methods can be divided into macroscopic methods which are sensitive to long-range diffusion
and into microscopic methods which give access to microscopic diffusion parameters like hopping rates of atoms or ions and the barrier heights for the jump processes.

<table>
<thead>
<tr>
<th></th>
<th>Macroscopic</th>
<th>Microscopic</th>
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<tbody>
<tr>
<td><strong>Nuclear</strong></td>
<td>Tracer diffusion</td>
<td>Quasielastic neutron scattering</td>
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<td></td>
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<td>Mössbauer spectroscopy</td>
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<td><strong>Non Nuclear</strong></td>
<td>DC conductivity</td>
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<td>Conductivity relaxation</td>
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Table 1. Some macroscopic/microscopic and nuclear/non-nuclear methods for studying diffusion in solids

Combining the results of macroscopic and microscopic methods one is able to evaluate the information about the observed diffusion mechanism. Furthermore it depends on the specific frequency range of each method whether preferably long-range or short-range diffusion is probed (fig.1). $\tau$ has been converted to $D$ via equation (1) adopting a typical jump length in solids of a few Å.

Up to now the diffusion in perovskite related compounds had been studied by means of electrical conductivity and modestly by relaxation experiments. When applicable, additional methods like QENS are needed, this can give deeper insight into the diffusion mechanisms. The experimental study of the dynamics of fast ionic conductors is fundamental for an understanding of the interactions between those ions and their lattice environment. The conduction mechanism in the perovskite-like compounds has been discussed [8, 9] and the intense debate focused on the relevance of a possible dynamic coupling between the rotational and translational motion of oxygen ions.

In this thesis the relation between the macroscopic ion transport and the microscopic diffusion mode in (Ca, Sr, Ba)(Ti, Fe)O$_{3-\delta}$ perovskite materials is established and combined with static (structural) investigations. The materials are examined at ambient and elevated temperatures using a broad spectrum of solid state experimental techniques such as: x-ray and neutron diffraction, microprobe analysis, Mössbauer spectroscopy, dc conductivity and quasielastic neutron scattering. A new model is developed to extract an ionic conductivity from resistivity relaxation data in a mixed conductor.
Fig. 1. Typical ranges of the diffusivity $D$ and of the motional correlation time $\tau$ for some macroscopic and microscopic methods to study diffusion in solids.
Chapter 1

Theoretical background

This thesis deals with non-stoichiometric (Ca, Sr, Ba)(Ti, Fe)O$_{3.5}$ perovskite compounds and the purpose of the first two chapters is to familiarize the reader with these materials including their potential for applications. Obviously the most interesting are those which can be directly used in our everyday life. The material becomes a mixed ionic-electronic conductor at evaluated temperatures by means of doping, i.e. replacing tetravalent Ti by trivalent Fe. For a given composition oxygen non-stoichiometry is determined by oxygen partial pressure and temperature. The equilibrium relationship of the oxygen non-stoichiometry with respect to the internal condition is critical to many applications. A possible use of those oxides in the fuel cells and as oxygen separation membranes, their structure and up to date knowledge will be briefly described. This chapter will also describe an innovative theory of the oxygen mobility determination due to the vacancies involved by means of quasielastic neutron scattering.

1.1. What is a fuel cell?

A most general and simple definition of a fuel cell is: ‘an electrochemical device that directly converts chemical energy from a reaction between a fuel and an oxidant into electrical energy’. They offer a clean, pollution free technology to electrochemically generated electricity at high efficiencies. The fuel cell can trace its roots back to the 1800’s. Oxford educated scientist, Sir William Robert Grove, realized that, if electrolysis using electricity could split water into hydrogen and oxygen, then the opposite would also be true. To test his reasoning, Sir Grove built a device that would combine hydrogen and oxygen to produce electricity, the world’s first gas battery. Today, most vehicles based on fuel cells rely on internal combustion engines and are significant producers of harmful gaseous emissions. Miniaturised fuel cells could offer a great advantage over conventional solid batteries for the military. Alkaline fuel cells had been already used onboard by NASA in the Space Shuttles. The most developed market for fuel cells at present is as stationary sources of electricity and heat.
The basic elements of a typical fuel cell are shown in fig. 1.1. Every fuel cell has two electrodes, one positive and one negative, called, the cathode and anode, respectively. Fuel cell also has an electrolyte, which carries electrically charged particles from one electrode to another. The fuel and oxidant gases flow along the surface of the anode and cathode, respectively, and they react electrochemically in the three-phase-boundary region established at the gas - electrolyte - electrode interface. Hydrogen is the basic fuel, but fuel cells also require oxygen.

1.2. Oxygen production techniques

Because oxygen is a component of air, it has been studied over the centuries and there are a large number of different methods for its preparation [10]. Earlier commercial plans for oxygen preparation used either catalytic decomposition of solid potassium chlorate \((2 \text{ KClO}_3 \rightarrow 2 \text{ KCl} + 3 \text{ O}_2)\) or the catalytic decomposition of hydrogen peroxide \((2 \text{ H}_2\text{O}_2 \rightarrow 2 \text{ HO}_2 + \text{ O}_2)\). Around the beginning of the 20th century, significant improvements were made in vacuum and gas compression techniques. This development enabled the refrigeration of air to its liquid state. Liquid air is a mixture of liquid nitrogen, boiling point \(\approx 196^\circ\text{C}\), and liquid oxygen, boiling point \(\approx183^\circ\text{C}\). The nitrogen is more volatile (i.e. it has a lower boiling point) and boils off first during evaporation. Some oxygen evaporates with the nitrogen. The nitrogen rich vapour can be
pumped off, leaving the fluid enriched with oxygen. This is the basis of oxygen production through cryogenic air distillation.

Pressure swing adsorption is another production technique for oxygen. It is based on the preferential absorption of nitrogen on adsorbents such as zeolites. The absorption process leaves the gas oxygen enriched. After the gas is stored in a container, the adsorbents are heated to release the nitrogen enriched gas. This process can be repeated until the desired purity of the oxygen is reached.

1.3. Mixed ionic electronic conducting membranes

An innovative method of oxygen production is by membrane separation from air using oxygen ion conductors with far greater efficiency and at one-third lower costs than the cryogenic processing technology used today. Currently, many oxygen ion conductors are developed to match a variety of needs imposed by applications. The crystal structures of these oxidic materials show empty lattice sites for oxygen ions, so-called vacancies. At elevated temperatures, an oxygen ion can jump into an oxygen vacancy. If in the new vicinity of the oxygen ion another vacancy is present, the ion can make a subsequent jump. In this way, the oxygen ions are rendered mobile. The above way of ionic transport is called a vacancy mechanism, as opposed to transport of oxygen ions over interstitial sites. In most oxygen ion conductors known to date, oxygen transport occurs through the vacancy mechanism. Many materials show ionic conductivity. Apart from oxygen ion conductivity, e.g. conduction of ions of sodium, silver, copper, lithium and fluorine have also been reported [11]. In the present thesis, the term ‘ionic conductivity’ is reserved for the conductivity of oxygen ions, unless an explicit exception is made.

Oxygen ions may not be the only mobile charge carriers in oxygen ion conductors. Electrons or electron holes may cause significant electric conduction. Compounds showing both ionic and electronic conductivity are called mixed ionic electronic conductors (MIECs). They find application as electrodes for oxygen pumps and SOFCs, but also in membranes for the separation of oxygen from air, see fig. 1.3. A MIEC membrane is semi permeable for oxygen gas with a theoretical separation factor of 100%. Under thermodynamical equilibrium, the oxygen partial pressures on the permeate side of a MIEC membrane will be equal to the partial pressure on the feed side where air is supplied. However, an oxygen partial pressure difference can be
created by pumping away the pure oxygen gas at the permeate side. This is the basis for the driving mechanism for sustained oxygen transport.

The net transport of oxygen through the membrane encompasses several processes (fig.1.3). On the air side (high oxygen partial pressure), the bond of the oxygen molecules is broken. The surface process involves the uptake of electrons and the occupation of oxygen vacancies. The ionic oxygen species diffuses to the permeate side (low oxygen partial pressure), where they release their electrons to form oxygen molecules. The oxygen transport occurs electrochemically through the bulk of the compound.

![Fig. 1.3. Transport scheme of a mixed ionic electronic conductor membrane](image)

Determining whether and how much of some material moves into or out of a cell depends solely on the free energy of the material inside the cell \( G_{in} \) compared to its free energy outside the cell \( G_{out} \) at equilibrium (i.e. when there is no net change in amounts). Or, in other words, movement across the membrane depends on \( \Delta G_{\text{out-in}} \). So, when \( \Delta G = 0 \), no energy was expended to obtain the equilibrium situation; if \( \Delta G \) is a positive value, then energy is stored in the gradient, and if it has a negative value, then energy is required to form the gradient. For considerations, \( G \) can be expressed simply as [12, 13]:

\[
G = RT \ln(c) + qFE ,
\]  

where \( c= \) concentration (moles) 
\( E= \) potential (volts. Note: \( \Delta E \) is the membrane potential) 
\( q= \) charge or valence (if any) of the transported substance

The other symbols are constants:
$R=$ gas constant (8.3143 Joules/mole/degree)

$T=$ temperature (298 degrees Kelvin)

$F=$ Faraday (96490 Joules/mole/volt)

In other words, $G$ is equal to the sum of a concentration term plus an electrical term. Since $G_{out} - G_{in}$ (that is $\Delta G$) is of importance, equation (1.3.1) can be arranged in the following way:

$$\Delta G = (RT \ln(c_{out}) + zFE_{out}) - (RT \ln(c_{in}) + zFE_{in}),$$

which simplifies to:

$$\Delta G = (RT \ln\left(\frac{c_{out}}{c_{in}}\right) - zF \Delta E).$$

(1.3.3)

If $\Delta G = 0$ in equation (1.3.3), i.e. no energy is needed to account for the equilibrium values, then the equation reduces to:

$$\Delta E = \frac{RT}{zF} \ln\left(\frac{c_{out}}{c_{in}}\right).$$

(1.3.4)

Applying equation (1.3.4) to the case of the oxygen permeable membrane, one obtains the electrical potential:

$$\Delta E = \frac{RT}{4F} \ln\left(\frac{P_{O_2}^{II}}{P_{O_2}^{I}}\right).$$

(1.3.5)

Eq. (1.3.5) is a Nernst equation which is used to calculate the equilibrium potential required to balance an ion concentration (or oxygen partial pressure) difference across a membrane.

The positive pole is at the interface with the higher oxygen partial pressure $P_{O_2}^{II}$. If $P_{O_2}^{II}$ is known and taken as a reference, the unknown value $P_{O_2}^{I}$ can be computed from this equation.

1.4. Electrical conductivity

Many properties of oxides are determined by or depend on the atomic and electronic transport properties. The fast transport of oxygen in dense ceramic membranes is an interesting and unusual phenomenon.

The name fast ionic conductor of oxygen implies electrical ionic conductivity on the order of 1 S cm$^{-1}$. For a material to achieve such high values of conductivity a large number of mobile ionic carriers must be present in the lattice. A high number can be achieved in a number of ways; however, the essence is to obtain a structure which contains a large number of equivalent sites for the mobile ion and which are only partially occupied.
At any temperature a crystal contains different structural imperfections or defects. If the imperfection is limited to one structural or lattice site, it is termed a point defect. Simple defects of this type include (1) empty sites or vacancies where the constituent atoms are missing in the structure or (2) interstitial atoms occupying the interstices between the regular sides. Point defects are responsible for the lattice diffusion and the point defects of the first type will be taken into account as a basis for further detailed considerations of the defect structure, the diffusion and the defect-controlled properties for the discussions in subsequent chapters.

1.4.1. Neutral and charged defects. Electroneutrality.

In a crystal the atoms are charged, and the cations and the anions may be assigned a definite valence. For the oxides, the oxygen ions on regular sites are considered to have a valence of -2. The cations have a positive valence such that the sum of all positive and negative charges in the compound becomes zero.

When vacancies are present and thus when atoms on regular sites are missing, part or all of the actual charge of the missing atom may also be absent from the vacant site. Let us consider the formation of an oxygen vacancy. In this case an oxygen atom on a normal site is removed from the crystal. In this process the two negative actual charges, i.e., two electrons, of the oxygen ion are left in the crystal.

From another hand, if an oxygen is introduced into the structure on the vacant oxygen site, two electrons are picked up and two holes are created.

Substitutionally dissolved foreign ions which have a valence different from that of normal ions (aliovalent foreign ions) will affect the distribution of the total charge. Lower valent substitutionally dissolved cations result in ‘free’ electrons in the lattice.

Quasi free electron and holes in the crystal, $e'$ and $h$ respectively, have to obey to the electroneutrality principle [14]:

$$\sum h = \sum e'. \quad (1.4.1.1)$$

This is a basic equation and condition for treating defect equilibria and for the evaluating defect concentrations in a crystal.
1.4.2. Total electrical conductivity of a mixed conductor

The total conductivity of a mixed conductor is the sum of the partial conductivities of ions $\sigma_{\text{ion}}$, excess electrons $\sigma_e$ and electron holes $\sigma_h$

$$\sigma_{\text{total}} = \sigma_{\text{ion}} + \sigma_e + \sigma_h.$$  \hspace{1cm} (1.4.2.1)

In order to combine the partial conductivities with oxygen partial pressure, the following models are discussed:

(a) if the chemical potential in the surrounding gas atmosphere is decreased, oxygen is removed from the lattice. By this reaction, oxygen vacancies $V'_o$ and an excess of electrons $e'$ are formed [15, 16]:

$$O'_o = V'_o + 2e' + \frac{1}{2}O_2.$$  \hspace{1cm} (1.4.2.2)

If equilibrium between the gas phase and the oxide is established there is no interaction between the charge defects. The mass action law [16-18] applied to reaction (1.4.2.2) yields in terms of concentrations:

$$[e'] = K[V'_o]^{\frac{1}{2}}P_{O_2}^{-\frac{1}{4}}.$$  \hspace{1cm} (1.4.2.3)

Two different cases may be considered:

(i) According to the reaction (1.4.2.2), the concentration of oxygen vacancies is one half of the concentration of the electrons. This is true if the concentrations of all other defects are sufficiently small. With this condition, it follows from eq. (1.4.2.3)

$$[e'] = K'P_{O_2}^{-\frac{1}{2}}.$$  \hspace{1cm} (1.4.2.4)

In general, the mobility of electrons exceeds by far that of the ionic species. The transference number of electrons (the fraction of the total current that is carried by electrons during electrolysis) is therefore close to unity in an oxide with equivalent concentration of oxygen vacancies and excess of electrons (n-type conductor). Such materials are not useful for purposes of galvanic cell measurements.

(ii) Alternatively, the concentration of oxygen vacancies can be fixed at a comparatively high level by chemical doping. The conductivity is then predominantly ionic in character. Only at very small oxygen pressures electrons also contribute to the electrical conduction. Since the concentration of oxygen vacancies is fixed by doping, eq. (1.4.2.3) reduces to:
The partial conductivity $\sigma_e$ is proportional to the concentration and to the mobility of electrons. If it is assumed that the mobility is not a function of oxygen pressure it follows that

$$\sigma_e \propto [e'] \propto P_{O_2}^{-1/4}.$$  \hspace{1cm} (1.4.2.6)

(b) The other limiting case is when at large oxygen potentials in the gas phase an excess of oxygen is accommodating in the lattice of the oxide. The defects produced are interstitial oxygen ions $O_i^*$ or cation vacancies $V_{Me}^*$. Electron holes are formed according to the electrical neutrality principle:

$$\frac{1}{2} O_2 = O_i^* + 2h$$  \hspace{1cm} (1.4.2.7)

or

$$\frac{1}{2} O_2 = V_{Me}^* + 2h + MeO.$$  \hspace{1cm} (1.4.2.8)

When the relations $[O_i^*] = \frac{1}{2} [h]$ or $[V_{Me}^*] = \frac{1}{2} [h]$ are valid, the concentration of electron holes is proportional to $P_{O_2}^{-1/6}$ in both cases. By the same argument as in section (a) (i), the material is predominantly a p-type conductor and thus unsuited for oxygen concentration cells.

If the concentration of oxygen vacancies is large as a result of chemical doping, the free lattice sites are occupied according to the reaction

$$\frac{1}{2} O_2 + V_{O}^{**} = O_o + 2h.$$  \hspace{1cm} (1.4.2.9)

Since $[V_{O}^{**}]$ is nearly constant, the following holds:

$$[h] = K'' P_{O_2}^{-1/2}.$$  \hspace{1cm} (1.4.2.10)

Then the partial conductivity by electron holes is described by

$$\sigma_e \propto [h] \propto P_{O_2}^{-1/4},$$  \hspace{1cm} (1.4.2.11)

when the same procedure and suppositions as in the proceeding section are used.

Eq. (1) may be expressed in terms of oxygen partial pressures for the oxide with a high oxygen defect concentration

$$\sigma_{\text{total}}(T, P_{O_2}) = \sigma_{\text{ion}}(T) + \sigma_e^0(T) P_{O_2}^{-1/4} + \sigma_h^0(T) P_{O_2}^{1/4},$$  \hspace{1cm} (1.4.2.12)
where the indexes \( \text{ion} \), \( e \) and \( h \) are related to the ion, electron and hole components of the total conductivity respectively, and \( \sigma_j^0 (j=n, p) \) corresponds to the values of partial conductivities at \( P_{O2}=1 \text{ atm} \).

1.4.3. Ionic conductivity

In the following the parameters pertaining to oxygen ion conductivity are derived and the important atomistic parameters are examined.

Let us consider a crystal with \( N \) equivalent sites per unit volume, which are partially occupied. One can define the occupied fraction as \( c \) and consequently the fraction of unoccupied sites becomes \( (1-c) \) [19, 20]. To move through the crystal the ions must be able to move into an unoccupied equivalent site with minimum hindrance. Clearly for the ion to be able to move easily from one equivalent site to another requires the height of the intervening energy barrier, \( \Delta G_m \), to be small.

The Einstein equation relates the ionic mobility \( \mu \) to the ionic self-diffusion coefficient \( D \) (in cm\(^2\) s\(^{-1}\)) [21]:

\[
\mu = \frac{q \cdot D}{k \cdot T} . \tag{1.4.3.1}
\]

The self-diffusion coefficient can be expanded by consideration of random walk theory in a 3d lattice to give [22]:

\[
D = \frac{z}{6} \cdot f \cdot (1-c) \cdot a_0^2 \cdot \nu_0 \cdot \exp\left(-\frac{\Delta G_m}{kT}\right), \tag{1.4.3.2}
\]

where \( z \) is the number of equivalent near neighbour sites, \( a_0 \) is the distance between equivalent sites, \( \nu_0 \) is a characteristic lattice frequency and \( \Delta G_m \) is a free energy of migration. The factor \( f \) is called the correlation factor, and represents the deviation from randomness of the atomic jumps. From electrodynamics law is:

\[
\Delta G_m = \Delta H_m - T \cdot \Delta S_m, \tag{1.4.3.3}
\]

where \( \Delta H_m \) is the migration enthalpy and \( \Delta S_m \) the entropy of migration. Defining the term \( \gamma \) as follows

\[
\gamma = \frac{z}{6} \cdot f \cdot \exp\left(\frac{\Delta S_m}{k}\right), \tag{1.4.3.4}
\]
1. THEORETICAL BACKGROUND

\[
\mu = \frac{q}{kT} \cdot \gamma \cdot (1-c) \cdot a_0^2 \cdot V_0 \cdot \exp\left\{\frac{-\Delta H_m}{kT}\right\}.
\]

(1.4.3.5)

Obviously the migration enthalpy, \(\Delta H_m\), is an important parameter as it dominates the temperature dependence of the ionic mobility.

The final expression for the ionic conductivity is obtained from:

\[
\sigma = n \cdot q \cdot \mu
\]

by recognising that the volume concentration of mobile ions, \(n\), is given by the product of \(N\) and \(c\). Thus,

\[
\sigma = N \cdot \frac{q^2}{kT} \cdot \gamma \cdot c \cdot (1-c) \cdot a_0^2 \cdot V_0 \cdot \exp\left\{\frac{-\Delta H_m}{kT}\right\}.
\]

(1.4.3.7)

Equating \((1-c)\) with the fraction of mobile oxygen vacancies, \(\left[ V_o \right]\), (expressed as a site fraction), gives the alternative expression, specific to oxide ion conductors:

\[
\sigma = N \cdot \frac{q^2}{kT} \cdot \gamma \cdot \left[ V_o \right] (1-\left[ V_o \right]) \cdot a_0^2 \cdot V_0 \cdot \exp\left\{\frac{-\Delta H_m}{kT}\right\}.
\]

(1.4.3.8)

This expression can be compared with the empirical relationship for conductivity:

\[
\sigma = \frac{\sigma_0}{T} \exp\left\{\frac{-E_a}{kT}\right\}.
\]

(1.4.3.9)

Eq. (1.4.3.7) is only appropriate provided the fraction of mobile ions in the \(c(1-c)\) term is independent of the temperature. Inspection of eq. (1.4.3.7) or (1.4.3.8) for \(\sigma\) reveals surprisingly few variables for the optimization of the ionic conductivity. Some of these terms are constants, e.g., \(q\), \(k\) and others, e.g., \(N\), \(\gamma\), \(a_0\), \(V_0\) are not expected to alter substantially from oxide to oxide. This leaves \(c\) and \(\Delta H_m\) as the important factors for the determination of the level of ionic conductivity. Note, that the predicted concentration dependence for the isothermal conductivity depends upon the \(c(1-c)\) term, and should follow the shape shown in fig. 1.4.3. For small values of \(c\) the conductivity increases with an approximately linear dependence. At higher concentrations a broad maximum in the conductivity occurs when the oxygen sublattice is half occupied.
Often, the ionic conductivity is not readily measurable for a mixed conductor. Thus the quantity of most use for comparison is the oxygen self-diffusion coefficient $D$ which can be determined by electrical conductivity relaxation technique.

1.4.4. Oxygen self-diffusion

The electrical conductivity relaxation technique is an efficient way to explore the oxidation and reduction kinetics and thus to study the oxygen mass transport. When the sample is subjected to a sudden change of $P_{O_2}$ in the surrounding atmosphere, oxygen is incorporated or released from the crystal lattice. In the relaxation process, nonstoichiometry spreads through the sample by lattice diffusion, which is driven by concentration gradients of the defects. The change of the conductivity with time is followed until a new thermodynamic equilibrium state is reached. Oxygen diffusion in mixed ionic electronic conductors involves the exchange reaction at the surface gas-solid and the oxygen ion diffusion through the bulk. Theoretical equations derived for the bulk diffusion and surface reaction can be fitted to the conductivity data obtained experimentally.

For many mixed conducting materials a change in the oxygen partial pressure will result in a corresponding change in the electrical conductivity of the material due to a change in the concentration of charge carriers. If the ionic conductivity of a material is significantly smaller
than its electronic conductivity then the time required for this change to propagate throughout the material is dominated by the bulk movement of the ionic species.

The diffusion process of the oxygen ions is described by Fick’s second law [23-25]:

\[
\frac{\partial C}{\partial t} = \text{div}(D \cdot \text{grad}C),
\]

(1.4.4.1)

where \( D \) is the oxygen diffusion coefficient and \( C \) is the concentration of the diffusing substance. Under the assumption of constant diffusion coefficient, in the 1d case the following equation holds:

\[
\frac{dC}{dt} = D \frac{d^2C}{dx^2}.
\]

(1.4.4.2)

Considering a thin sample slab of thickness \( 2l \) (fig. 1.4.4.1), the initial and boundary conditions are

\[
C(x,0) = C_0
\]

(1.4.4.3)

\[
\frac{dC}{dx} \bigg|_{x=0} = 0,
\]

(1.4.4.4)

where \( C_0 \) is the initial concentration of oxide ions in the sample. Without considering the surface effect, another boundary condition for the outer surface can be written as

\[
C(\pm l, t) = C_{\infty},
\]

(1.4.4.5)

where \( C_{\infty} \) is the final concentration of oxide ions in the sample. The analytical solution to eq. (1.4.4.2) with conditions (1.4.4.3)-(1.4.4.5) is given by Crank [26]:

\[
\frac{M(t)}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot \exp \left[ - \frac{(2n+1)^2 \pi^2 D_{\text{chem}} t}{4l^2} \right]
\]

(1.4.4.6)

\( \frac{M(t)}{M_{\infty}} \) represents the ratio between the total amount of diffused substance at time \( t \) and at time infinity.

Fig. 1.4.4.1. Definition of the sample geometry.
Conductivity change and $\frac{M(t)}{M_\infty}$ are related as described in the following [27-29]. Considering the shadowed fraction of sample slab (fig. 1.4.4.2a), the resistance due to the $j$th charge carrier is given by

$$dR_j = \rho_j \frac{L}{Wdx} = \frac{1}{\sigma_j} \frac{L}{Wdx} = \frac{1}{C_j Z_j q \mu_j} \frac{L}{Wdx},$$

(1.4.4.7)

where $\rho_j$ is the resistivity of the $j$th charge carrier (in $\Omega$ cm), $\sigma_j$ is the conductivity of the $j$th charge carrier (in S cm$^{-1}$), $C_j$ is the concentration of the $j$th charge carrier (in cm$^{-3}$), $q$ is the elementary charge (in C), $Z_j$ is the number of the elementary charge carried by the $j$th charge carrier, $\mu_j$ is the mobility of the $j$th charge carrier (in cm$^2$ V$^{-1}$ s$^{-1}$), $L$ and $W$ are length and width of the sample slab (in cm). Resistance due to all kinds of conducting species is given by

$$dR = \frac{1}{\sum_j (dR_j)^{-1}} = \frac{1}{\sum_j C_j Z_j q \mu_j} \frac{L}{Wdx}.$$

(1.4.4.8)

During the re-equilibration process, there is a distribution of resistance within the sample. The equivalent circuit is given by a parallel connection of variable-resistance elements, as shown in fig. 1.4.4.2b. Thus, the overall resistance is

$$R = \left(\sum \frac{1}{dR}\right)^{-1} = \left[ \int \sum_j C_j(x) Z_j q \mu_j \frac{Wdx}{L} \right]^{-1} = \left[ \sum_j Z_j q \mu_j \frac{W}{L} \int C_j(x) dx \right]^{-1}.$$

(1.4.4.9)

If the atmosphere change is not very large such that the conduction mechanism does not change during the re-equilibration and taking into account the electroneutrality condition of the system eq. (1.4.1.1) then:

$$C(x) \approx C_j(x).$$

(1.4.4.10)

Thus, the apparent conductivity can be expressed as
The integral gives \( N_o \), the total number of charge carrier (oxygen ions) in the sample slab. It is related to the mass change ratio of diffusion substance by

\[
\frac{M_j}{M_\infty} = \frac{N_o(t) - N_o(0)}{N_o(\infty) - N_o(0)} = \frac{N_h(t) - N_h(0)}{N_h(\infty) - N_h(0)} = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)},
\]

(1.4.4.11)

where \( N_h \) is the total number of holes in the sample. To obtain the above equation, the assumption of constant mobility (mobility irrespective of the carrier concentration) was used. This leads to the expression of time change of the conductivity as

\[
\frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = 1 - \sum_{n=1}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-\frac{(2n+1)^2 \pi^2 D_{chem} t}{4l^2}\right].
\]

(1.4.4.12)

Least squares fitting of the relaxation data to this equation allows to determine the diffusion coefficient \( D \).

Electrical conductivity measurements permit access to the dynamical properties on a macroscopic scale, which compliment neutron studies which look at related properties on an atomic scale.

### 1.5. Neutron scattering

The neutron is an elementary particle with a mass of \( m_n = 1.6 \cdot 10^{-27} \) kg [30]. The kinetic energy of the neutron with mass \( m_n \) and speed \( v_n \) is

\[
E_n = \frac{1}{2} m_n v_n^2.
\]

(1.5.1)

Neutrons also can be considered as plane waves \( |\psi_0\rangle = e^{ikz} \) with wave vector \( \vec{k} = \frac{m}{h} \vec{v} \) and wavelength \( \lambda = \frac{2\pi}{|\vec{k}|} = \frac{h}{mv_n} \), so that the kinetic energy of a neutron can be equally written:

\[
E_n = \frac{\hbar^2 k^2}{2m_n} = \frac{h^2}{2m_n \lambda^2}.
\]

(1.5.2)

Thermal neutrons, corresponding to \( T \sim 300K \), have an energy of \( \sim 25\text{meV} \) and wavelength of \( 1.8\text{Å} \).
Thermal neutrons are a powerful probe for condensed matter systems, and are able to give simultaneously information on atomic structures and atomic motions. This is because neutrons possess a unique combination of properties:

**Wavelength:** thermal neutrons have wavelengths in the range 0.1 Å - 10 Å, which match typical interatomic separations in condensed matter systems. Thus thermal neutrons are able to probe the atomic arrangements in these systems.

**Energy:** neutrons have energies in the range 1 meV - 300 meV, which match the energies of many excitations existing in condensed matter systems. Thus thermal neutrons are able to measure the energies of these atomic motions.

**Magnetism:** Neutrons have a magnetic moment and interact with the magnetization in materials on the atomic scale. The neutron carries a spin of $\frac{1}{2}$ which is accompanied by a magnetic dipole moment:

$$\mu_n = -1.913 \mu_N,$$

(1.5.3)

where $\mu_N$ is the nuclear magneton.

**Selectivity:** neutrons interact with the nucleus of an atom rather than with its electron distribution, and the strength of the interaction is specified by a single quantity, the neutron scattering length. It is independent of the chemical environment in which the nucleus is situated, and it is independent of the scattering angle and of the neutron energy. The scattering length is not a monoatomic function of atomic number (fig. 1.5.1). Neighbouring elements in the periodic table and even isotopes of the same element may have very different cross sections. Neutrons are thus sensitive to light atoms in the presence of heavy ones and they are suited to application of the technique of isotopic substitution.

**Neutrality:** Neutrons are non-destructive and highly penetrating. They probe the interior of bulk materials, independent of the surface condition. Consequently, the use of complex sample environments such as cryostats, furnaces, pressure cells etc. is routine.

In following the main aspects of neutron scattering will be given.

Fig. 1.5.1. The dependence of the total neutron scattering lengths as a function of atomic number.
1.5.1. Scattering experiment

When neutrons are scattered by matter, the process can alter both the momentum and the energy of the neutron (fig.1.5.1.1). The energy transfer, \( \hbar \omega \), between the initial, \( E_0 \), and final, \( E \), energies of neutrons can be described as:

\[
\hbar \omega = E - E_0 = \frac{\hbar^2}{2m} (k^2 - k_0^2),
\]

where \( \vec{k} \) and \( \vec{k}_0 \) are the corresponding wave vectors. The corresponding wave vector transfer \( \vec{Q} \) is:

\[
\vec{Q} = \vec{k} - \vec{k}_0.
\]

Elastic neutron scattering is scattering with no change in neutron energy, i.e. with \( \hbar \omega = 0 \), and inelastic neutron scattering is scattering with a change in neutron energy, i.e. with \( \hbar \omega \neq 0 \). On the other hand, quasielastic neutron scattering (QENS) is a scattering phenomenon which is centred at zero energy transfer but which introduces a broadening of the spectral width due to the diffusive motions.

1.5.2. Scattering cross-sections

As mentioned the neutron nucleus scattering is isotropic and characterised by a single parameter, \( b \), the scattering length. This parameter is independent of the neutron energy. \( b \) can be
complex and the real part can be positive or negative according to the attractive or repulsive nature of the interaction. The imaginary part of $b$ represents absorption.

In experiments, the specimen is composed of several atomic species, $i$, often each of them being a mixture of several isotopes with nuclear spin. The scattering length, $b_i$, changes not only from species to species but also for isotopes of the same species.

The average $\langle b_i \rangle$ of $b_i$ over all the isotopes and spin states is called the coherent scattering length of an element. The incoherent scattering length is defined as the root mean square deviation of $b_i$ from $\langle b_i \rangle$:

\[
\begin{align*}
&b_{i,\text{coh}} = \langle b_i \rangle, \\
&b_{i,\text{inc}} = \left[\langle b_i^2 \rangle - \langle b_i \rangle^2\right]^{1/2}.
\end{align*}
\]

In the case of a single isotope, with nuclear spin $s$ interacting with a neutron spin $\frac{1}{2}$, the two scattering length are $b^+$ and $b^-$ associated with two possible spin states, $S^+ = s + \frac{1}{2}$ and $S^- = s - \frac{1}{2}$. Because there are $n^+ = 2S^+ + 1$ and $n^- = 2S^- + 1$ states of spin for $S^+$ and $S^-$, respectively. Each of them has the same probability,

\[
\begin{align*}
&\langle b \rangle = \frac{1}{n^+ + n^-} \left[n^+ b^+ + n^- b^-\right], \\
&b_{\text{inc}} = \frac{1}{2s + 1} \left[(s+1)b^+ + sb^-\right], \\
&\langle b^2 \rangle = \frac{1}{n^+ + n^-} \left[n^+ (b^+)^2 + n^- (b^-)^2\right] = \frac{1}{2s + 1} \left[(s+1)(b^+)^2 + s(b^-)^2\right].
\end{align*}
\]

These expressions permit the evaluation of the coherent cross section defined as

\[
\sigma_{\text{coh}} = 4\pi\langle b \rangle^2
\]

and incoherent cross section:

\[
\sigma_{\text{inc}} = 4\pi\left(\langle b^2 \rangle - \langle b \rangle^2\right) = 4\pi\langle (b - \langle b \rangle)^2 \rangle.
\]

Then the total scattering cross section is

\[
\sigma_{\text{total}} = \sigma_{\text{coh}} + \sigma_{\text{inc}}.
\]
1.5.3. Scattering by a condensed matter, scattering functions

The quantity measured in neutron scattering is the double differential cross section which represents the intensity scattered with energy $E$ with momentum $k$ into a solid angle $\Omega$, and is given by (fig. 1.5.3.1) [31]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{k}{k_0} \left( \frac{\sigma_{coh}}{4\pi} S_{coh}(Q, \omega) + \frac{\sigma_{incoh}}{4\pi} S_{incoh}(Q, \omega) \right).$$

The double differential cross section gives the probability for a neutron to go from an initial state with energy $E_0$ to the final state with energy $E$.

There are terms in eq. (1.5.3.1) arising from the different cross sections as emphasized above (eq. (1.5.2.8)). First, the constant prefactors $\frac{\sigma_{coh}}{4\pi}$ and $\frac{\sigma_{incoh}}{4\pi}$ are properties of the neutron-target interaction. They allow one to select between coherent and incoherent processes, depending on the isotopes present in the target. Second, the scattering functions $S_{coh}(Q, \omega)$ and $S_{incoh}(Q, \omega)$ depend on the properties of the sample. The scattering functions can be related to the space and time correlation functions of the particles in the target. This formalism goes back to Van Hove [36]. A derivation can be found in any standard text on the theory of thermal neutron scattering [30, 34, 35, 46]. Here the main results are quoted.

The correlation function $G(\vec{r}, t) dt$ is the conditional probability that a given particle was at time $t=0$ at the origin $r=0$, any particle is found at time $t$ at the position $\vec{r}$ in the volume element $d\vec{r}'$:

$$G(\vec{r}, t) = \frac{1}{N} \left\{ d\vec{r}' \sum_i \delta(\vec{r}' - \vec{R}_i(0)) \delta(\vec{r}' - \vec{R}_i(t)) \right\}. \quad (1.5.3.2)$$

'Any particle' means the same or different particle, i.e. correlation function contains a self and a distinct part.
1. THEORETICAL BACKGROUND

\[ G(\vec{r},t) = G(\vec{r}) + G'(\vec{r},t). \]  \hspace{1cm} (1.5.3.3)

\( G(\vec{r}) \) represents the static pair distribution function, which is well-known from X-ray diffraction: it can be interpreted as the probability of finding any particle in the unit volume around position \( \vec{r} \), if another particle is at the origin, \( i \neq j \), and this function does not depend on time. \( G'(\vec{r},t) \) is a self correlation function which expresses the probability that, given a particle at the origin \( \vec{r} = 0 \) at time \( t=0 \), it is to be found at the position \( \vec{r} \) at time \( t \).

The correlation functions fulfil the normalization requirement:

\[ \int G(\vec{r})d\vec{r} = N, \]  \hspace{1cm} (1.5.3.4)

\[ \int G'(\vec{r},t)d\vec{r} = 1. \]  \hspace{1cm} (1.5.3.5)

Thus the coherent scattering function \( S_{coh}(Q,\omega) \) is the space and time Fourier transform of the pair-correlation function. With coherent neutron scattering, collective phenomena such as Bragg reflections can be observed. By integrating the coherent scattering function over all energies, one obtains the structure factor:

\[ S_{coh}(\vec{Q}) = \int S_{coh}(\vec{Q},\omega)d\omega. \]  \hspace{1cm} (1.5.3.6)

Given the translational symmetry of a crystal, the coherent structure factor consists of the set of \( \delta \)-functions at Bragg positions.

The incoherent scattering function, being the space and time Fourier transform of the self-correlation function, does not exhibit any interference phenomena. Energy integration of the incoherent scattering function yields:

\[ S_{inc}(\vec{Q}) = \int S_{inc}(\vec{Q},\omega)d\omega = 1. \]  \hspace{1cm} (1.5.3.7)

For diffusive motions, the particles are distributed in space in a random fashion. At time zero, it can be assumed that the atom is at a particular site with probability of 1. With time increase, this probability will either decrease to 0 (if atoms diffuse to infinity) or it will decrease to a finite value (if the particle remains in the restricted volume). Thus, the self-correlation function can be broken into two parts:

\[ G'(\vec{r},t) = G'(\vec{r}) + G''(\vec{r},t), \]  \hspace{1cm} (1.5.3.8)

where \( G'(\vec{r}) \) gives the probability of finding the considered atom at infinite time at a distance \( \vec{r} \) from its starting point. It is a time independent function and its Fourier transform is elastic in energy. With respect to the time-dependent part of the self correlation function, \( G''(\vec{r},t) \), it is assumed that it decays exponentially towards its limiting value \( G'(\vec{r}) \). Thus the measured spectrum will be composed of elastic and quasielastic components, and the incoherent scattering function has a form:
1. THEORETICAL BACKGROUND

\[ S_{\text{inc}}(\vec{Q}, \omega) = A_0(\vec{Q})\delta(\omega) + (1 - A_0(\vec{Q})) \frac{\Gamma/\pi}{\Gamma^2 + \omega^2}, \]  

(1.5.3.9)

where \(A_0(\vec{Q})\) is the elastic incoherent structure factor (EISF), which provides an important information related to the geometry of the diffusive path, and \(\Gamma\) is the width of the Lorentzian function describing the quasielastic component and relates to the decay constant.

The width of the QENS is proportional to the diffusivity of the particles. To relate this quasielastic neutron scattering to particular particle motion is the topic of the next chapter.

1.5.4. Diffusive scattering

**Translations diffusion:’ long range’**

The basic equation governing diffusion is Frick’s law eq.(1.4.4.1) which describes jump processes macroscopically. In the microscopic limit the self-correlation function obeys the equation:

\[ \frac{\partial}{\partial t} G'(\vec{r},t) = D\vec{\nabla}^2 G'(\vec{r},t). \]  

(1.5.4.1)

With the initial conditions \(G'(\vec{r},0) = \delta\) and integrating over all space \(\int G'(\vec{r},t) d\vec{r} = 1\), the solution is

\[ G'(\vec{r},t) = \frac{1}{(4\pi D t)^{3/2}} e^{-r^2/(4Dt)}. \]  

(1.5.4.2)

The Fourier transformation of this function in both space \(Q\) and time \(t\) leads to the intermediate scattering function:

\[ I(\vec{Q},t) = \int G'(\vec{r},t) \exp(i\vec{Q} \cdot \vec{r}) d\vec{r} = \exp(-D\vec{Q}^2 t) \]  

(1.5.4.3)

and the scattering function [31, 34]:

\[ S_{\text{inc}}(\vec{Q}, \omega) = \frac{1}{\pi} \frac{D\vec{Q}^2}{\omega^2 + (D\vec{Q}^2)^2}. \]  

(1.5.4.4)

Thus, in the case of a diffusive motion the quasielastic line exhibits a Lorenzian shape and the full width half maximum (FWHM) is:

\[ 2\Gamma = 2\hbar D\vec{Q}^2. \]  

(1.5.4.5)

At sufficiently small \(Q\) this so called \(Q^2\) law is generally valid irrespective of the details of the diffusion mechanism and single particle diffusion extending over ‘large’ distances \(\vec{r}\) is observed.
Translational diffusion in Bravais lattice

At larger $Q$ values incoherent quasielastic neutron data contain information on the diffusion mechanism. In many materials atoms diffuse in the presence of vacancies. These vacancies diffuse rapidly through the lattice and each jump of the vacancy is connected with a jump of a lattice atom. It is assumed that the jumps are instantaneous, i.e. the mean residence time $\tau$ of a particle at a given lattice site is much longer than the flight time to the next lattice site at the distance $\bar{l}$. As a consequence, for incoherent scattering of the nuclei in the lattice, the quasi elastic spectrum can be calculated in the framework of the Chudley-Elliott model [39] and the probability of finding the particle at $\bar{r}$ at time $t$:

$$\frac{\partial P(\bar{r}, t)}{\partial t} = \frac{1}{z \tau} \sum_{i} [P(\bar{r} + \bar{l}_i, t) - P(\bar{r}, t)],$$

where the sum is taken over all $z$ next nearest neighbour sites at distance $\bar{l}_i$. With the boundary conditions $P(\bar{r}, 0) = \delta(\bar{r})$ the probability becomes equivalent to the self-correlation function $G'(\bar{r}, t)$. The Fourier transformation of eq.(1.5.4.6) with respect to space and with the definition of the self correlation function, the Lorenzian shaped scattering function is:

$$S_{inc}(\vec{Q}, \omega) = \frac{1}{\pi} \frac{f(\vec{Q})/\tau}{(f(\vec{Q})/\tau)^2 + \omega^2},$$

where

$$f(\vec{Q}) = \frac{1}{z} \sum_{i=1}^{n} (1 - e^{-i \vec{Q} \cdot \bar{l}_i}).$$

In this case the FWHM is determined as

$$2\Gamma = 2hf'(\vec{Q})/\tau.$$

Bravais lattices exhibit inversion symmetry, and each site is an inversion centre; therefore, for each jump vector $\bar{l}_i$ there exists a jump vector $-\bar{l}_i$, and the sum over $n$ exponential functions gives a sum over $n/2$ cosine functions.

Let us consider the limiting cases of small and large $Q$ values. For small $Q$ the exponential in eq.(1.5.4.8) is expanded up to the square term:

$$2\Gamma = \frac{2h}{n \tau} \sum_{i=1}^{n} (1 - 1 + i \bar{Q} \cdot \bar{l}_i + \frac{1}{2} (\bar{Q} \cdot \bar{l}_i)^2).$$

Let us denote $l = |\bar{l}_i|$ the mean jump length and take into account that the spatial average of $|\bar{Q} \cdot \bar{l}_i|$ gives $\frac{1}{3} Q^2 l^2$. Thus for small $Q$:
Thus the Chadley-Elliott model transforms into the $Q^2$ law for small $Q$.

For large $Q$ values, the line width is oscillating with $Q$. Assuming that an atom or molecule is located on a site and from time to time performs a jump to a neighbouring site and the jump length $l$ is identical for all sites, whereas the jump direction is random. Thus a spatially averaged eq. (1.5.4.8) becomes:

$$2\Gamma = \frac{2h l^2}{6\tau} Q^2 = 2h D Q^2. \quad (1.5.4.11)$$

This function is plotted in Fig (1.5.5.1). For small Q values the sin function can be expanded, resulting in a $Q^2$ law.

**Rotational diffusion**

Here particles constrained to instantaneous jumps in the lattice are considered. In contrast to the translational diffusion, the particle is forced to stay within a defined volume and the self correlation function retains a finite component to infinite times. The FWHM of the Lorenzian component is independent of the scattering vector in this case. In following the cases of two and $N$ equivalent sites are described [31, 40-43].

- **Neutron scattering law for two equivalent sites:**

The simplest case is a so called dumb-bell, where the particle jumps back and forth between two isoenergetical sites. For rotational motion, the incoherent scattering law in general can be written...
with the help of eq. (1.5.3.9) where the half width at half maximum of the Lorentzian function is inversely proportional to the residence time:

\[ S(Q, \omega) = A_0(Q) \delta(\omega) + A_1(Q) \frac{1}{\pi} \frac{2\tau}{4 + \omega^2 \tau^2}, \]  

(1.5.4.13)

where \( A_0(Q) \) is the elastic incoherent structure factor and \( A_1(Q) \) is the quasielastic incoherent structure factor for a jump motion over two equivalent sites. The structure factors fulfil the relation

\[ A_0(Q) + A_1(Q) = 1. \]  

(1.5.4.14)

For the powder samples, when the average is taken over all possible orientations of the \( Q \) vector, the structure factors are defined as:

\[ A_0(Q) = \frac{1}{2} [1 + j_0(Ql)], \]  

(1.5.4.15)

\[ A_1(Q) = \frac{1}{2} [1 - j_0(Ql)], \]  

(1.5.4.16)

where \( j_0(x) \) is a Bessel function of zero order and \( l = |r_2 - r_1| \) is the jump distance between two sites.

- **Jump model among \( N \) equivalent sites**

In this model it is assumed that a particle is located at the \( i \)th site among \( N \) equivalent sites equally distributed in a circle of radius \( r \). The resulting expression of the scattering law for a powder sample is

\[ S_{inc}(Q, \omega) = A_0(Q) \delta(\omega) + \sum_{i=1}^{N} A_i(Q) \frac{1}{\pi} \frac{\tau_i}{1 + \omega^2 \tau_i^2}, \]  

(1.5.4.17)

with

\[ A_0(Q) = \frac{1}{N} \sum_{n=1}^{N} j_0(Q \cdot r_n), \]  

(1.5.4.18)

\[ A_i(Q) = \frac{1}{N} \sum_{n=1}^{N} j_0(Q \cdot r_n) \cos \left( \frac{2l \cdot n \cdot \pi}{N} \right). \]  

(1.5.4.19)

The \( r_n \) are the jump distances

\[ r_n = 2r \sin \left( \frac{n\pi}{N} \right). \]  

(1.5.4.20)
1.5.5. Oxygen vacancy induced diffusion

Solid ionic conductors and mixed conductors form the basic materials of solid state ionics due to their important properties resulting from ion mobility. The most fundamental property of mixed conductors is their ionic conductivity, and this is connected to the diffusivity via the Nernst Einstein equation. Therefore QENS studies can significantly contribute to an understanding of the atomistic mechanism of ionic transport in solids; however, due to the limited energy resolution of neutron spectrometers only ions with exceptionally high ionic mobilities and thus with rather small ionic radii and light atomic mass are suited for the QENS investigations. For this reason $\mathrm{H}^+$, $\mathrm{Li}^+$, $\mathrm{Na}^+$, $\mathrm{Cu}^+$ are good cation candidates and $\mathrm{O}^{2-}$, $\mathrm{OH}^-$, $\mathrm{H}^-$, $\mathrm{F}^-$, $\mathrm{Cl}^-$ are anion candidates for fast ionic mobility (table 1.5.5.1) [44, 45]. The second requirement is favourable neutron scattering properties, i.e. large $\sigma_{\text{incoh}}$ and small absorption cross-sections.

<table>
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<th>$\sigma_{\text{incoh}},\text{barns}$</th>
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</tr>
<tr>
<td>Cl$^-$</td>
<td>1.81</td>
<td>11.53</td>
<td>5.2</td>
<td>33.5</td>
</tr>
</tbody>
</table>

Table 1.5.5.1. Ionic radii, coherent, incoherent neutron scattering cross-sections and neutron absorption cross-sections for possible fast conducting ions [44, 45].

Last but not least, the structure of solid ionic conductors has to fulfil the requirement that the mobile ion only partially occupies the lattice sites on its sublattice. This can be achieved by several ways described in the 1.4 Electrical conductivity section. Here we consider the case when the sample has oxygen diffusion due to the introduction of oxygen vacancies.

A particular problem for the experiment is the small scattering cross section from oxygen, which becomes larger due to introducing oxygen vacancies and thus can be estimated as Laue diffuse scattering. Oxygen is considered as a practically pure coherent scatterer [44, table 1.5.5.1]. Under the condition of a statistical distribution of oxygen vacancies, this cross section
appears like an incoherent scattering contribution. The cross sections can be estimated according to the following considerations.

As it was shown earlier the total scattering cross section which describes the neutron-target interaction is \( \sigma_{\text{total}} = 4 \cdot \pi \cdot b^2 \), where \( b \) is a scattering length. Usually the target contains isotopes with individual scattering lengths (earlier in section 1.5.2 Scattering experiment). Under all practical conditions the isotopes are randomly distributed which introduces disorder scattering, also called incoherent scattering (actually, spin disorder is another cause of incoherent scattering, which we need not consider further in this context). In the case of two isotopes with scattering length \( b_1 \) and \( b_2 \) with concentrations \( c_1 \) and \( c_2 \) and with \( c_1 + c_2 = 1 \), the cross sections for total scattering \( \sigma_{\text{tot}} \), coherent scattering \( \sigma_{\text{coh}} \) and incoherent scattering \( \sigma_{\text{inc}} \) are

\[
\sigma_{\text{total}} = 4 \cdot \pi \cdot \left(b_1^2 + b_2^2\right),
\]

\[
\sigma_{\text{coh}} = 4 \cdot \pi \cdot b_1^2 = 4 \cdot \pi \cdot \left(c_1 b_1 + c_2 b_2\right),
\]

\[
\sigma_{\text{inc}} = \sigma_{\text{total}} - \sigma_{\text{coh}} = 4 \cdot \pi \cdot c_1 \cdot c_2 (b_1 - b_2)^2.
\]

We now assume that the oxygen lattice is occupied by two different isotopes, one with the scattering length of oxygen \( b_1 \) (occupied site), the other with a scattering length \( b_2 = 0 \) (oxygen defect). Modifying the eq. (1.5.5.3), one can obtain

\[
\sigma_{\text{inc}} = \sigma_{\text{total}} - \sigma_{\text{coh}} = 4 \cdot \pi \cdot c_1 \cdot (1 - c_1) \cdot (b_1 - b_2)^2.
\]

The term \( c(1-c) \) determines the shape of the total incoherent cross section dependence on the concentration of the occupied oxygen sites. (fig. 1.5.5.1.)

![Figure 1.5.5.1](image_url)

**Fig. 1.5.5.1.** Concentration dependence of the incoherent cross section predicted from eq. (1.5.5.4).

One can see the common features in dependences of the ionic conductivity and incoherent cross section on vacancies concentration (fig. 1.4.3, 1.5.5.1).
Chapter 2

Systems of investigation

2.1. Perovskite structure

A large group of mixed ionic electronic conductors adopts the ABO$_3$ perovskite structure. The atomic arrangement in this structure was first found for the mineral perovskite, CaTiO$_3$.

The ABO$_3$ structure can be described as a cubic array of corner-shared BO$_6$ octahedra. The A site ion resides between the BO$_6$ octahedra. The perovskite lattice can also be described by considering the cubic close packing of AO$_3$ with the B ions placed in the interlayer octahedral interstitial sites (fig. 2.1a) [47]. The A and O ions are approximately of the same size, while the B site ions tend to be much smaller. In order to have contact between the A, B and O ions, $R_A + R_O$ should be equal to $\sqrt{2}(R_B + R_O)$ where $R_A$, $R_B$, $R_O$ are the ionic radii. Goldschmidt [48] has shown that the cubic perovskite structure is stable only if a tolerance factor, $t$, defined by $R_A + R_O = t\sqrt{2}(R_B + R_O)$ has a value in the range 0.78<$t$<1.05, which is found to exist for the compounds in the perovskite family [49].

The real perovskite structure often deviates from the ideal cubic structure. Depending on the specific values of the ionic radii in real perovskite crystals, gaps between some ions always exist and hence there is some freedom for displacements of the ions. For example, the ideal perovskite structure is found for SrTiO$_3$ at room temperature; more usually the structure is modified by cation displacement as in BaTiO$_3$, or by tilting of octahedra as in CaTiO$_3$. The cation displacements, which are directly linked with ferroelectricity and antiferroelectricity, do not directly affect the lattice parameters except by a relatively small distortion of the octahedra. The tilting of octahedra has usually a far greater effect on lattice parameters.

Octahedral tilting in perovskites was first examined by Megaw and Darlington [50], and fundamental work was carried out by Glazer [51], demonstrating that the space group is determined largely by the pattern of in-space ($a^+$), anti-phase ($a^-$) and null ($a^0$) octahedral tilting along one of the Cartesian coordinate axes. A classification of octahedral tilting in terms of 23 alternative tilt systems was also proposed.
The general pattern of the perovskite structure is extremely tenacious and it persists over a wide range of cation substitutions, both isovalent and aliovalent. The response to aliovalent doping and to oxidation-reduction are linked, since reduction, the loss of oxygen from an oxide, reduces the average formal oxidation state of the cations, and is thus equivalent to substitution of a lower valence cation for one of the host cations. The extent of nonstoichiometry achieved by changes in the equilibrium oxygen activity depends very strongly on the chemical nature of the cation present. In order for oxide to undergo extensive reduction, for example, it must contain a cation that is easily reduced. For modest deviations from the ideal perovskite composition, the oxides typically respond by the formation of lattice defects distributed randomly throughout the matrix. For large deviations, on the other hand, the defects may order into a superstructure that maintains major elements of the perovskite structure. Thus the compositions over the entire range $A_2B_2O_5$ to $A_2B_2O_7$ may retain layers of various thicknesses having the perovskite structure, separated by layers of oxygen-deficiency or oxygen-excess. It is then convenient to organize compositions according to the O/A ratio, as shown in fig.2.2. [52]. For convenience, the case of SrTiO$_3$ is used.
Various perovskite compounds whose B sites are occupied by two cation species have been synthesized to date, and their crystal structures have been solved [53]. These compounds have the general chemical formula $\text{AB}_{1-x}\text{B}_x\text{O}_3$. When the difference in ionic radii or charges between two different B-site cations increases, ordering of the B-site cations may occur, giving rise to different crystal structures [54].

As it was shown above, both A and B sites may be occupied by more than one cation species in a particular compound. In the case of B-sites this can involve cations of more than one element, or it may involve two oxidation states of the same element. The physical properties of the compound will depend on whether or not cation ordering occurs.

Many properties of the crystal strongly depend on stoichiometry. The structural defects due to the deviation from stoichiometry of perovskite resulting from cationic doping are very important for electrical transport because high conductivity can be often ascribed to a high concentration of point defects obtained by doping with aliovalent cations. Cationic substitution with ions of a different oxidation state allows the creation of compounds changing from a complete anionic sublattice, i.e. the perovskite structure, to one with the concentration of oxygen defects of 0.5 per formula unit, i.e. the brownmillerite structure. A model for CaTiO$_{3-\delta}$ intermediate structures has been proposed by Grenier et al [55]. An original structural model of vacancy ordering consists of a sequence of n-1 (where n=1/y) sheets of octahedra alternating with one sheet of tetrahedra. The formation of tetrahedral sheets is due to the ordering of the oxygen vacancies along the (0k0) planes of the cubic perovskite structure.
Since advances in the development of ceramics rely on an understanding of the mechanisms that contribute to the formation of the microscopical features, it is very important from a scientific and technical point of view to control the defects (statically and dynamically) in the matrix, with the objective of obtaining the desired electrical and mechanical properties.

2.2. Structural issues and ionic conductivity of (Ca, Sr, Ba)(Ti, Fe)O$_{3-\delta}$ systems

Mixed ionic-electronic conductors of ATiO$_3$ (A=Ca, Sr, Ba) structure with partial substitution of titanium with iron are of current interest. Doping of oxygen-conducting ceramics with multivalent cations can lead to the simultaneous occurrence of ionic and electronic conductivity.

In several investigations [56-60] it has been shown that doping with acceptor impurities such as Fe at Ti-sites improves both the ionic and the electronic conductivity. The reaction of iron substitution in ATiO$_3$ may be written using Kröger-Vink notation [15]:

$$2AO + Fe_2O_3 = 2A_i^+ + 2Fe_\mathcal{T}^+ + 5O_\mathcal{V}^\cdot + V_\mathcal{O}^{**}.$$  \hspace{1cm} (2.2.1)

Based on this equation it is assumed that the electroneutrality condition may be approximated by

$$2[V_\mathcal{O}^{**}] = [Fe_\mathcal{T}^+] = constant.$$ \hspace{1cm} (2.2.2)

The formation of oxygen vacancies increases the ionic conductivity [56-61]. Although the oxygen ionic and electronic conductivities are moderate when compared to other perovskites such as (La, Sr)(Co, Fe)O$_{3-\delta}$ [61, 62], the superior stability of (Ca, Sr, Ba)(Fe, Ti)O$_{3-\delta}$ systems in reducing atmospheres and the moderate thermal expansion [63] are fundamental properties for high temperature technological applications.

2.2.1. CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system

The phase relations for the system CaO-TiO$_2$-Fe$_2$O$_3$ [64, 65] are given in fig. 2.2.1.1. The perovskite solid solution expressed as CaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ ends at $x = 0.67$. The theoretical Fe-end member CaFeO$_{2.5}$ is not a perovskite phase. It is expressed as Ca$_2$Fe$_2$O$_5$ and crystallises in the brownmillerite structure - oxygen deficient perovskite type, with an orthorhombic unit cell (fig.2.1b).

The structure of iron-substituted calcium titanates was extensively characterised by Grenier et al. [66-68]. The phases in the Ca(Ti, Fe)O$_{3-\delta}$ system may be seen as intermediates
between perovskite CaTiO$_3$ and brownmillerite Ca$_2$Fe$_2$O$_5$. The perovskite structure can be described as a sequence of FeO$_6$ octahedral layers. The brownmillerite structure is derived from the perovskite structure by replacing alternately one out of two octahedral layers by a tetrahedral one. The periodic distribution of FeO$_4$ tetrahedral layers is characteristic of intermediate compositions with the general formula CaTi$_{1-x}$Fe$_x$O$_{3-x/2}$, which can be seen as the result of ordered or disordered intergrowths of the original compounds. For $x<0.5$, the oxygen vacancies are randomly distributed or partly ordered in microdomains with finite length size; the CaTiO$_3$ orthorhombic structure is preserved. For $x \geq 0.5$, long-range ordering appears, leading to the formation of fully ordered new phases. The fully ordered phases can be described by the general formula $A_nB_nO_{3n-1}$, where $n$ is an integer. Compositional variations in these and other nonstoichiometric perovskites are often accommodated by the formation of microdomains in complex structural arrangements [66-69]. The degree of ordering in the oxygen sublattice will determine the concentration and mobility of oxygen vacancies available for ion hopping and, thus, for ionic conductivity.

In [70-74] the appearance was reported of high ionic conductivity for the CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system at evaluated temperatures. However, a maximum for the ionic conductivity on iron substitution content was observed (ca. $x=0.2$). [75, 76] reported on the origin of such conduction behaviour. The detailed mechanism and type of oxygen vacancy ordering as a function of

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**Fig. 2.2.1.1. Sub-solidus phase relations in the system CaO-Fe$_2$O$_3$-TiO$_2$ in air ($P_{O_2}=0.21$ atm)**

In [70-74] the appearance was reported of high ionic conductivity for the CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system at evaluated temperatures. However, a maximum for the ionic conductivity on iron substitution content was observed (ca. $x=0.2$). [75, 76] reported on the origin of such conduction behaviour. The detailed mechanism and type of oxygen vacancy ordering as a function of
annealing temperature and composition in the system CaTiO₃-CaFeO₂.₅ was investigated by X-ray diffraction, high-resolution transmission electron microscopy and Mössbauer spectroscopy. The abrupt change in the ionic conductivity was interpreted by an order-disorder transition in the oxygen sublattice causing a change from high mobility of charge carriers present as small clusters in the disordered region, to a reduced mobility of charge carriers due to the formation of vacancy bearing layers in the partially ordered phases. Also, the order-disorder transition represents a change from three-dimensional to one-dimensional conductivity. The corresponding phase diagram for CaTiO₃ → CaFeO₂.₅ is shown in fig. 2.2.1.2 [72]. In the region labelled ‘disordered’ no correlated arrangement of oxygen vacancies is found. At moderate Fe contents and for lower temperatures the vacancies become partially ordered into chains of infinite length (region labelled ‘partially ordered’), while fully ordered structures with a regular sequence of octahedral (O) and tetrahedral (T) layers develop at x=0.5 (TOOO structure), x=0.667 (TOO structure) and at x=1 (TO structure). The structure of the oxygen vacancies has a pronounced influence on transport properties such as electrical conductivity.

Fig. 2.2.1.2. Phase diagram for the system CaTiO₃-CaFeO₂.₅ as a function of temperature and composition [72]. Symbols TO, TOO and TOOO describe the fully ordered structure types (sequence of tetrahedral and octahedral layers). The bold line defines the order-disorder phase transition.
2.2.2. $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ system

The system $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ was first synthesized by Clevenger [77] who interpreted the electronic properties in terms of an electron-hopping mechanism occurring between the $\text{Fe}^{3+}$-$\text{Fe}^{4+}$ pairs existing in a solid matrix. Brixner [78] has also studied this system but with samples synthesised in a reducing atmosphere, and reached the same conclusions as Clevenger with respect to the conductivity of the perovskite samples. However, up to now there is no accepted explanation for the spatial distribution of the oxygen vacancies in this system.

The phase diagram of the $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ system is not well established and the published data are inconsistent. According to [79] the transition of the end member $\text{Sr}_2\text{Fe}_2\text{O}_5$ from the low temperature ordered form (brownmillerite structure) to the high temperature disordered form (perovskite structure) observed at about 850°C was explained by microdomain formation. The structure at intermediate concentrations of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (with $x=0.8$) shows superstructures due to 2D ordering of vacancies which could be identified by high resolution TEM observations [80]. Steinsvik et al. [81] investigated ordering in the system with $x=0.0-0.8$ by TEM and electron diffraction. For $x<0.5$ only the cubic perovskite structure was found. Also, they observed the ordering of oxygen vacancies with $x=0.6$ and $x=0.8$ quenched form 1000°C under oxidizing and reducing atmospheres. In contrast, Rodriguez [82] did not observe any superstructure lines using x-ray or by electron diffraction and also electron microscopy did not provide any evidence for oxygen vacancy ordering. These negative results in looking for the superstructure spots indicate that a) the anionic vacancies are randomly distributed or b) in the case of the existence of some ordering it would not be periodic and its contribution to the diffraction patterns would appear in an incoherent background between Bragg reflections. Moreover, the conductivity data in [81] show the increase of conductivity values with iron content ($x=0.0-0.8$) as predicted from a simple defect model in which the oxygen vacancy charges compensate for the substitution of titanium by iron. Such conductivity behaviour is in contradiction with the $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ system where the maximum in conductivity is an indication for a phase transition. More accurate examination of the $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ system is needed to discuss transport and structural properties within a common picture.

2.2.3. $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ system

The $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ system presents a mixed conduction mechanism with both ionic and electronic conductivities ($n$- and $p$-type) at elevated temperatures like the $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_3$. 
δ and the SrTi$_{1-x}$Fe$_x$O$_{3-δ}$ systems (fig.2.2.3.1). The electrical conductivity of the BaTi$_{1-x}$Fe$_x$O$_{3-δ}$ system was investigated in [83]. The ionic conductivity at $x=0.2$ at $T=1000^\circ C$ exceeds the conductivity by one order of magnitude compared to the compounds with $x=0.1$ and $x=0.3$. One can assume that an order-disorder transition in the oxygen sublattice occurs, similar to the ionic conductivity as found in the system CaTi$_{1-x}$Fe$_x$O$_{3-δ}$ (2.2.1. CaTi$_{1-x}$Fe$_x$O$_{3-δ}$ system section). In general, the tendency to form ordered structures progressively grows with increasing defect concentration. An ordering phenomenon usually greatly reduces the ion conductivity as observed for $x=0.3$. However, the data show a renewed increase of ionic conductivity at higher values of $x$. The possible reason for such behavior may be related with abrupt changes in the oxygen occupation function and the Fe$^{4+}$ content.

The unit cell can be described as 6 pseudo-close-packed BaO$_3$ layers which form a (cch)$_2$ sequence, i.e. [Ba(2)O(2)]$_2$Ba(2)O(2)Ba(1)O(1)]. Atoms Ti(1) and Ti(2) occupy corner- and face-sharing octahedra respectively, with rather short Ti(2)–Ti(2) distances in the face sharing Ti$_2$O$_9$ octahedra (fig. 2.2.3.2) [84, 85]. When Ti$^{4+}$ is substituted by Fe$^{3+}$, oxygen vacancies are created according to the electroneutrality condition [Fe$^{3+}$] = 2[V$^{\dot{\cdot}}_O$] so that the oxygen is removed only from the O(1) sites in the Ba(1)O(1) layers.

![Graph showing the dependence of ionic conductivity on iron content at T=1000°C](image)

Fig.2.2.3.1. Dependence of ionic conductivity on iron content at $T=1000^\circ C$ for:
1- SrTi$_{1-x}$Fe$_x$O$_{3-δ}$ system [81]
2- BaTi$_{1-x}$Fe$_x$O$_{3-δ}$ system [83]
3- CaTi$_{1-x}$Fe$_x$O$_{3-δ}$ system [71, 72]
2. SYSTEMS OF INVESTIGATION

There is an extensive solid solution of $6H$-$\text{BaTi}_1-x\text{Fe}_x\text{O}_{3-\delta}$ that extends to ca. $x=0.67$ (fig. 2.2.3.3), depending on temperature and oxygen fugacity [86, 87]. Close to the $\text{BaTiO}_3$ end member, $\text{Fe}^{3+}$ is stable over a wide range of oxygen partial pressures (from $10^{-4}$ to $10^{-22}$ bar at 700°C) [87], while $\text{Fe}^{4+}$ becomes more stable relative to $\text{Fe}^{3+}$ under oxidizing conditions as the iron concentration increases [86].

![Crystal structure of $6H$-$\text{BaTi}_1-x\text{Fe}_x\text{O}_{3-\delta}$](image1)

There is an extensive solid solution of $6H$-$\text{BaTi}_1-x\text{Fe}_x\text{O}_{3-\delta}$ that extends to ca. $x=0.67$ (fig. 2.2.3.3), depending on temperature and oxygen fugacity [86, 87]. Close to the $\text{BaTiO}_3$ end member, $\text{Fe}^{3+}$ is stable over a wide range of oxygen partial pressures (from $10^{-4}$ to $10^{-22}$ bar at 700°C) [87], while $\text{Fe}^{4+}$ becomes more stable relative to $\text{Fe}^{3+}$ under oxidizing conditions as the iron concentration increases [86].

![BaO–Fe$_2$O$_3$–TiO$_2$ phase diagram (air, 1250–1270°C)](image2)
2. SYSTEMS OF INVESTIGATION

There is limited Mössbauer data for BaTi$_{1-x}$Fe$_x$O$_{3.5}$. Studies near the BaTiO$_3$ endmember focused on the behaviour of Fe$^{4+}$, and consequently found it difficult to prepare samples except under highly oxidizing conditions [88, 89]. Fe$^{4+}$ occurred as a quadrupole doublet at room temperature with a narrow linewidth and a centre shift (relative to $\alpha$-Fe) of -0.01 mm/s, while Fe$^{3+}$ could only be resolved as a broad quadrupole doublet with a centre shift (relative to $\alpha$-Fe) about 0.3 mm/s [88]. At the other endmember, studies of BaFeO$_{2.95}$ reported similar results: a narrow quadrupole doublet assigned to Fe$^{4+}$ at room temperature with a centre shift (relative to $\alpha$-Fe) of -0.06 mm/s and a broad quadrupole doublet assigned to Fe$^{3+}$ with a centre shift (relative to $\alpha$-Fe) near 0.5 mm/s [90]. None of the studies were able to resolve the Fe$^{3+}$ quadrupole doublet sufficiently to determine the Fe$^{3+}$ site distribution.

Since the structural properties play an essential role for the physical properties, binding together the microscopic and macroscopic properties is important.
Chapter 3

Experimental techniques

This chapter provides a brief description of experimental methods used in the thesis. The information is presented in short form and further details can be found in textbooks and specialized monographs cited in the text.

The materials were studied using a wide range of experimental methods covering different aspects of structure and diffusion dynamics. The crystal structure was investigated using X-ray and neutron powder diffraction at ambient and elevated temperatures. The structural study was enhanced by Mössbauer experiments. The phase examination and non-stoichiometry was investigated by microprobe analysis. The dynamic properties were studied by electrical conductivity and quasielastic neutron scattering.

3.1. Static properties

• X-ray diffraction

The X-rays are diffracted according to Bragg’s law:

\[ 2d \cdot \sin \Theta = n\lambda \],

where \( \Theta \) is the Bragg angle and \( \lambda \) is the wavelength of the X-rays which are reflected from net planes formed by the crystal lattice of the material. By varying the angle of incidence, a diffraction pattern emerges which is characteristic for the sample. The pattern is identified by comparing it with an internationally recognized data base containing tens of thousands of reference patterns [91-93].

X-ray diffraction measurements were performed to characterize the structure of the sample and phase analysis. X-ray intensity data were collected on a Siemens D-5000 diffractometer using Cu \( K_\alpha \) radiation. Step scan intensity measurements were made in the \( 2\theta \) range 20° to 80° at intervals of 0.02°.
• Neutron diffraction

Neutron diffraction provides similar structural information as x-ray diffraction but the interaction between the projectile and matter is different [94, 95] (1.5. Neutron scattering section). Photons interact predominantly with the electrons and nuclear scattering can be neglected. Neutrons interact with the nucleus via the nuclear force and with the magnetic moment of unpaired electrons via the electromagnetic ones. Consequently, the techniques of X-rays diffraction and neutron diffraction are complimentary and in the present applications, neutron scattering yields information not accessible using x-rays. Neutron diffraction had been performed on the spectrometer D20 (ILL, France) [96] with an incident wavelength of 1.3Å to study the structural and magnetic properties of SrTi$_{1-x}$Fe$_x$O$_{3-x/2}$ system.

• Mössbauer spectroscopy

Mössbauer spectroscopy is a type of nuclear spectroscopy involving the resonant emission and absorption of γ-rays (i.e., the Mössbauer effect) [97, 98]. This effect requires a "recoil-free" nuclear transition, i.e., a nuclear transition in which no net change in momentum is imparted to the nucleus. Secondly, the energy of the source photon must be exactly identical to the nuclear transition energy in the absorber (i.e., the sample being analyzed). The probability for a recoil-free transition increases with the rigidity of the source and absorber and thus is highest for solids at low temperatures. In conventional instruments, the energy of the source photon is varied over a small range (tens of neV) using the Doppler effect (fig.3.1.1). The source is repetitively accelerated through a range in velocities (from a few to hundreds of mm s$^{-1}$) to add or subtract energy to the photons being emitted. When a match in the energy of the source photon and the absorber transition energy is achieved, resonant absorption occurs. Because subsequent emission of the absorbed photon has no directional probability in contrast to the source photon directed at the detector, a decrease in the intensity of the background signal is observed at the energies (velocities) where resonant absorption occurs (fig. 3.1.2).
Although more than half of the elements in the periodic table have isotopes exhibiting the Mössbauer effect, the $^{57}\text{Fe}$ isotope is the most favorable isotope for Mössbauer spectroscopy. This is because

a) the recoil energy associated with absorption of the $\gamma$-rays of 14.41 keV ($I = 3/2$ to $I = 1/2$ transition) is low

b) the half-width of the resonant line is narrow (3 x $10^{-13}$ times the energy of the $\gamma$-rays)

c) the natural abundance of $^{57}\text{Fe}$ is high (2.14%)

The main advantage of $^{57}\text{Fe}$ Mössbauer spectroscopy is that it is a Fe-specific technique with greater sensitivity than X-ray diffraction. For example, Fe oxidation states and local
environments are identifiable for samples with Fe contents as low as 0.5 wt.% if samples enriched in $^{57}$Fe are used.

The interactions between the nucleus and the atomic electrons depend strongly on the electronic, chemical and magnetic state of the atom. Information from these hyperfine interactions is provided by the hyperfine parameters which can be determined experimentally from the line positions in a Mössbauer spectrum. The following sections give a brief description of the parameters.

- **Isomer Shift (IS)**

The isomer shift $\delta$ is a result of the differences in the electronic densities at the nucleus between the emitting and the absorbing atoms. The difference changes the Mössbauer transition energy and the spectrum is shifted. IS (in mm/s) can be expressed using the following formula:

$$\delta = C \frac{\Delta R}{R} \left( |\psi(0)|^2 - |\psi(0)|^2 \right),$$  \hspace{1cm} (3.1.2)

where $C$ is constant, $R$ is the effective nuclear radius, $|\psi(0)|^2 - |\psi(0)|^2$ is the difference in electron density at the nucleus in absorber and the source respectively [98]. The $\Delta R$ denotes the difference in the nuclear radius between the exited and the ground state. Eq. (3.1.2) shows that the shift is sensitive to the electronic surrounding of the nucleus, in particular the changes affecting s shells which have a finite electron density at the nucleus. The isomer shift only alters the energy levels and its value is obtained directly from the position of the absorption line.

- **Quadrupole Splitting (QS)**

The quadrupole splitting $\Delta$ is a result of the interaction of the nuclear quadrupole moment with the electric field gradient. The quadrupole moment $Q$ is characteristic for each state/isotope. The splitting of the energy levels can be expressed using the following formula:

$$\Delta = eQV_{zz},$$  \hspace{1cm} (3.1.3)

where $V_{zz}$ is the largest component of the electric gradient. The energy level split creates a doublet in the Mössbauer spectrum.

- **Magnetic splitting**
A nucleus with quantum spin number $I$ has $2I+1$ degenerate energy levels. They become separated upon the introduction of an external or internal magnetic field $B$ due to the Zeeman effect. The $2I+1$ states are described by quantum numbers $m_I$:

$$m_I = -I, -I + 1, ..., I - 1, I$$

and their energies are shifted from the zero field value by a value given by the formula:

$$\Delta E = -g\mu_N Bm_I,$$

where $\mu_N = \frac{e\hbar}{2m_p}$ is a nuclear magneton, $m_p$ is the proton mass and $g$ is the nuclear Landé factor.

The magnetic field splits the $I=1/2$ state into two energy levels and the $I=3/2$ state into four separate levels. However, the selection rules allow only six possible transitions between these levels and the splitting appears as a sextet instead of an octet in the Mössbauer spectrum.

Mössbauer spectra were recorded at room temperature (293 K) in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 1.85 GBq $^{57}$Co source in a 6 micron Rh matrix. Spectra took typically three days each to collect. The velocity scale was calibrated relative to 25 µm α-Fe foil using the positions certified for National Bureau of Standards standard reference material no. 1541; line widths of 0.28 mm/s for the outer lines of α-Fe were obtained at room temperature. The spectra were fitted to Lorentzian lineshapes using the commercially available fitting program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany).

Samples for Mössbauer spectroscopy were prepared by mixing powdered materials with benzophenone and mounting in Plexiglass sample holders. Sample weights were calculated to provide the optimum sample thickness while minimising thickness effects due to absorption [99], and varied from 1 to 5 mg Fe/cm$^2$.

A Mössbauer study of oxygen vacancy and cation distribution in 6H-BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ had been evaluated. The iron oxidation state in SrTi$_{1-x}$Fe$_x$O$_{3-x/2}$ system after drop quenching was studied by means of Mössbauer spectroscopy.

- Microprobe analysis

Electron microprobe analysis [100, 101] is a technique for chemically analyzing small selected areas of solid samples, in which x-rays are excited by a focused electron beam. Qualitative analysis involves the identification of the lines in the spectrum and it is fairly straightforward owing to the simplicity of the X-ray spectra. Quantitative analysis (determination
of the concentration of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration standards of known composition.

By scanning the beam in a television-like raster and displaying the intensity of selected X-ray line, element distribution images or ‘maps’ can be produced. Images produced by electrons collected from the sample reveal mean atomic number difference (fig.3.1.2.3. a) or surface topography (fig. 3.1.2.3 b) according to the mode selected.

Microprobe analysis has been used for the phase analysis and non-stoichiometry studies. The data were collected using a JXA-8200 Super Probe (JEOL) microprobe with an applied voltage and current of 15 kV and 25 nA, respectively. All samples for this analysis were mounted in an epoxy resin, cut, polished and coated with a conductive layer of carbon. Characteristic X-ray emission intensities of the specific elements, as measured in the microprobe, were converted to chemical weight percents and molar ratios.

![Fig. 3.1.2.3. Backscattered (a) and secondary (b) electron image of SrTi_{0.5}Fe_{0.5}O_{3-δ}. Left picture represents mean atomic element distribution, right- the surface morphology.](image)

3.2. **Dynamic properties**

- Quasielastic neutron scattering

The neutron spectroscopy methods consist of the measurement of changes in both energy and momentum of neutrons interacting with matter in order to obtain the information about the dynamics and the geometry of constituent atoms.
Any instrument used to carry out quasielastic neutron scattering experiments, on a steady state source, must perform three functions:

1. the incident neutrons must be selected from the white beam from the reactor core in a small range between $E_0$ and $E_0 + dE$ and in a small angle about the direction $k_0$.
2. the final energy $E$ of the scattered neutrons must be analysed to determine the energy change $\hbar \omega = E - E_0$.
3. the scattering angle with respect to the incident beam and with respect to the sample orientation must be measured to determine the momentum transfer $\mathbf{Q} = \mathbf{k} - \mathbf{k}_0$.

The specifications of each instrument are: the incident energy, the energy resolution, the accessible $Q$-range, the $Q$-resolution and the flux at the sample. Quasielastic neutron spectra have been measured by time-of-flight spectrometry on IN5 (ILL, Grenoble), FOCUS (PSI, Switzerland) with resolutions in the range of about 0.01 to 0.1 meV and by µeV resolution backscattering spectrometry at IN10, IN16 (ILL, Grenoble), HFBS (NIST, USA). The detailed description of the spectrometers can be found on the web-pages of the institutes [102].

In following the common principles of the instruments will be given in brief.

**Time-of-flight spectrometer**

The time-of-flight chopper spectrometers [103, 104] allow the determination of the final neutron energies through a direct measurement of their velocities (fig. 3.2.1.). The monochromator selects a particular energy $E_0$ from the incoming white neutron beam. Then the continuous and monochromatic neutron flux is chopped in short bursts to set a time mark $t=0$ for the flight time of the neutrons from the chopper to the detectors. Arrays of detectors are placed in the scattering plane to simultaneously collect counts for several wave-vectors. Each detector is connected with a multichannel analyser to register the total flight time of the neutron burst:

$$t_0 = \frac{m}{2} \left( \frac{L_1}{\sqrt{E_0}} + \frac{L_2}{\sqrt{E}} \right),$$  (3.2.1)
where \( m \) is the mass of neutron, \( L_1 \) and \( L_2 \) are the distances between chopper-sample and sample-detector, respectively. For \( t_0 \neq \left( \frac{m}{2E_0} \right)^{\frac{1}{2}} (L_1 + L_2) \) the neutrons are scattered inelastically in the target, where a larger value represents neutron energy loss and a smaller value energy gain. Obviously, the registration of the energy loss part of the spectrum is limited by the time intervals between two bursts. Larger flight times lead to frame overlaps.

The energy resolution of ToF is given by

\[
\Delta E = \frac{2\Delta t}{t} E_0, \quad (3.2.2)
\]

where the duration of the pulses \( \Delta t \) is inversely proportional to the chopper speed \( S \), \( t = CL\lambda \) is the flight time for elastic scattering, with \( C=252.7 \mu \text{sec/meter} \text{Å} \), \( L=L_1+L_2 \), and \( E_0=1/\lambda^2 \) is the neutron energy. Therefore the resolution is proportional to

\[
\Delta E = \text{const} / SL\lambda^3. \quad (3.2.3)
\]

Thus the resolution can be improved by using a long flight path and a long wavelength. Resolutions of 9.4\( \mu \)eV and 7\( \mu \)eV can be reached on IN5 (ILL, France) and FOCUS (PSI, Switzerland) ToF spectrometers respectively.

FOCUS has no chopper monochromator, it makes the beam monochromatic through reflection on a crystal (either graphite or mica). The pulsing is then performed through a Fermi chopper, i.e. a rotating slit package (fig.3.2.1)

---

**Fig. 3.2.1.** Schematic outline of a time of flight spectrometer like FOCUS
**Backscattering spectrometers**

Backscattering spectrometers [105, 106] measure the final energy of the neutrons which are detected in a narrow band of energy of about 1μeV. Conversely the initial energy of these neutrons is varied around this value. These spectrometers are suited to measure very small energy changes. The high-energy resolution is achieved by working with the largest possible Bragg angle at the monochromator and at the analyser crystals, $\theta_M=\theta_A=90^\circ$. Under these conditions, the Bragg-reflected wavelength band $\Delta \lambda$ becomes very narrow even for a large divergence $\Delta \theta$ of the neutron beam as shown in fig. 3.2.2, where the wavelength is plotted against the Bragg angle.

![Fig.3.2.2. The principle of high-resolution backscattering. Near $\theta=90^\circ$, the wavelength $\lambda$ changes only in second order with Bragg angle $\theta$.](image)

Differentiating the Bragg relation $\lambda = 2d \sin \theta$ to $\Delta \lambda = \frac{\partial \lambda}{\partial \theta} \Delta \theta + \frac{\partial \lambda}{\partial d} \Delta d$, and thus

$$\frac{\Delta \lambda}{\lambda} = \cot \theta \Delta \theta + \frac{1}{d} \Delta d$$

The expression of the energy resolution is deduced:

$$\frac{\Delta E}{E} = \frac{2 \Delta \lambda}{\lambda} = 2 \cot \theta \Delta \theta + \frac{2 \Delta d}{d}. \quad (3.2.4)$$

The $\cot \theta$ term is minimized by working close (within the divergence of the beam) to exact backscattering geometry ($\theta=90^\circ$). The second term only depends on the crystal quality. The energy of the incident neutrons can be varied either by a Doppler motion of the monochromator or by modifying the lattice parameters of the monochromator by cooling or heating. Only the neutrons which have lost in the sample the energy change given by one of those processes are reflected by the analyser crystals back into detectors. This situation is called “backscattering” which means that the incident and the Bragg reflected beams are practically antiparallel (fig.3.2.3).
3. EXPERIMENTAL TECHNIQUES

- **Fixed window scan**

Sometimes backscattering spectrometers are used with the Doppler drive at rest. For a Lorenzian shaped scattering law \( S(Q, \omega) = (\Gamma / \pi) / (\Gamma^2 + \omega^2) \) originated from a thermal activated process, one can obtain the spectral intensity integrated over the resolution width \( \Delta \omega \) of the monochromator. Assuming a rectangular resolution window, this leads to
\[
S(Q, \omega = 0, T) = (2 / \pi) \arctg \left[ \Delta \omega / 2 \Gamma(Q,T) \right] 
\]
where \( T \) is the sample temperature. For low temperatures, the quasielastic line falls into the energy window and one gets \( S_0(Q,0) = 1 \). With increasing temperature, the line width \( \Gamma \) becomes broader than the window \( \Delta \omega \), and the intensity reveals a stepwise decrease. Therefore, a simple temperature scan allows to get rapidly a quantitative survey of the diffusion processes in the sample as a function of temperature.

- **Electrical conductivity**

An electrical conductivity station has been built up for the investigation of dynamical properties. It is computer controlled for fully automated measurements using well established techniques like gas mixture stabilized fugacity and the four probe resistance method. The software has been written to include relaxation measurements for a sequence of different fugacities or temperature conditions. The accuracy of the oxygen gas flux (H\(_2\)/CO\(_2\) gas mixture) is 1 to 5 % (depending on the gas ratio), temperature fluctuations are controlled within \( \pm 0.5^\circ \text{C} \), and the resolution of the electronic characteristics are down to 1\( \mu \)V and 1\( \text{pA} \).
For electrical conductivity measurements, a rectangular shape sample was used. Four electrodes were deposited by using Pt paste and Pt wires. They were attached as current and voltage leads (fig. 3.2.4). The volume conductivity is calculated as follows:

\[ \sigma = \frac{I}{V \cdot \frac{l}{S}}, \]  

where \( I \) is applied current, \( V \) is measured voltage, \( l \) is the distance between the voltage leads, and \( S = a \cdot b \) is the cross section area of the measured sample.

The total electrical conductivity has been measured as a function of oxygen partial pressure and temperature.

Electrical relaxation conductivity experiments are relatively easy to perform. However, to obtain accurate data some practical issues must be considered. The diffusion equation for relaxation technique is solved assuming the instantaneous change in the oxygen partial pressure surrounding the specimen [26]. If this is not the case and the time of the step change in \( P_{O2} \) to occur is not insignificant for the conductivity change, then the relaxation profile will be altered and longer than expected. This can be considered by introducing of time delay in the relaxation process and thus the starting point for the data treatment has to be shifted by the time for oxygen delivery. Fig. 3.2.5 shows a typical profile of oxygen partial pressure. It takes approximately 260 seconds to deliver the oxygen in the measuring setup and this laps of time was subtracted when fitting relaxation data.
3. EXPERIMENTAL TECHNIQUES

- $H_2$-$CO_2$ gas mixture

Atmospheres for electrical conductivity measurements with various $P_{O_2}$ were achieved by using $H_2$/CO$_2$ gas mixtures. In the following the algebraic derivations of the necessary equations are presented in order to calculate the $P_{O_2}$ values produced at different temperatures [107].

Let the mole fraction $n_1$ of carbon dioxide be mixed with the mole fraction of hydrogen $n_2$, and subsequently let carbon dioxide dissociate into carbon monoxide according to the reaction:

$$CO_2 = CO + \frac{1}{2}O_2.$$  \hspace{1cm} (3.2.6)

Hydrogen will then react with oxygen to form water:

$$H_2 + \frac{1}{2}O_2 = H_2O.$$  \hspace{1cm} (3.2.7)

If the fraction $a$ of each mole of carbon dioxide dissociates to form oxygen, and the fraction $b$ of each mole of hydrogen reacts to form water, then the mole fraction of carbon dioxide left will be $n_1(1-a)$, the mole fraction of carbon monoxide formed is $n_1a$, the number of mole fractions left is $n_2(1-b)$, and the number of mole fractions of oxygen present is $\frac{1}{2}(n_1a-n_2b)$. The total number of mole fractions present are:

$$n_t = n_1(1+a/2) + n_2(1-b/2).$$  \hspace{1cm} (3.2.8)

For a total pressure of one atmosphere and with the mixing ratio defined for the $H_2$/CO$_2$ mixtures as $R_m=n_1/n_2$, the partial pressures of the five components present are expressed as follows:

$$P_{CO_2} = 2(1-a)/(2 + a + R_m(2-b)),$$  \hspace{1cm} (3.2.9)

$$P_{CO} = 2a/(2 + a + R_m(2-b)),$$  \hspace{1cm} (3.2.10)

$$P_{H_2} = 2R_m(1-b)/(2 + a + R_m(2-b)).$$  \hspace{1cm} (3.2.11)

Fig. 3.2.5. Typical step in oxygen partial pressure. Approximately 260 seconds are needed for the oxygen deliverance in the measuring setup.
3. EXPERIMENTAL TECHNIQUES

\[ P_{H_2O} = \frac{2R_m b}{2 + a + R_m (2 - b)}, \quad (3.2.12) \]

\[ P_{O_2} = \frac{(a - b)R_m}{2 + a + R_m (2 - b)}, \quad (3.2.13) \]

from which ‘a’ can be expressed with Eq. (3.2.9-10) and the equilibrium constant \( K_1 \):

\[ P_{CO_2} / P_{CO} = (1 - a) / a = P_{O_2}^{1/2} / K_1, \quad (3.2.14) \]

\[ a = K_1 / (K_1 + P_{O_2}^{1/2}) \quad (3.2.15) \]

and from which ‘b’ may be expressed using Eq. (3.2.11-13), and the equilibrium constant \( K_2 \):

\[ P_{H_2O} / P_{H_2} = \frac{b}{1 - b} = P_{O_2}^{1/2} / K_2, \quad (3.2.16) \]

\[ b = P_{O_2}^{1/2} / (K_2 + P_{O_2}^{1/2}). \quad (3.2.17) \]

Hence, for a given temperature (which determines the values of \( K_1 \) and \( K_2 \)) and any desired fugacity of oxygen, the fraction \( a \) and \( b \) can be computed from Eq. (3.2.16-17).

One can now express \( R_m \) in terms of \( a, b \) and \( P_{O_2} \) with the help of Eq. (3.2.15):

\[ R_m = \frac{(a(1 - P_{O_2}) - 2P_{O_2})}{(b(1 - P_{O_2}) + 2P_{O_2})}. \quad (3.2.18) \]

If one wants to determine the mixing ratio of hydrogen to carbon dioxide which is required to produce a desired equilibrium fugacity of oxygen, one should evaluate ‘a’ and ‘b’ from eq. (3.2.16-17) at that temperature and use Eq. (3.2.18) to compute the necessary mixing ratio to produce the desired fugacity of oxygen.

In this system the control of the fugacity of oxygen through variation of the mixing ratio \( H_2/CO_2 \) is no longer possible if the fugacity is equal to or falls below that of the equilibrium fugacity of oxygen for the reaction: \( CO_2 = C + O_2 \), thereby causing carbon precipitation.
Chapter 4

Sample preparation and characterization

Polycrystalline samples of CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (x=0.15, 0.3), SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (x=0.15, 0.3, 0.5, 0.8) and BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (x=0.1, 0.2, 0.3, 0.6) were prepared via solid state reaction [108]. Initial reagents of BaCO$_3$, CaCO$_3$, SrCO$_3$, Fe$_2$O$_3$ and TiO$_2$ (all from Aldrich Chem. Co., with 99.9% purity) powders were dried, then appropriately weighed and mixed in an agate mortar under ethanol for about 30 minutes. All compositions were calcinated at T=1000°C for 24 hours, then pressed into pellets and synthesized in air in a temperature range from T=1300°C to 1000°C for 140 to 72 hours (depending on composition, run times and temperatures, decreased with increasing iron concentration) with intermediate grinding and x-ray examination (Table 4.1). For electrical conductivity measurements all samples were pressed into rectangular bars of approximately the same size (4.9×2.0×17 mm). Pellets were fired subsequently then at 1350°C for 24-48 hours in air.

The phase purity was checked by powder x-ray diffraction at room temperature. Analysis of spectra showed single phase compositions, and the crystal structure and the unit cell parameters were identified using the Rietveld method. Data are compared with published results.

The microstructure of pressed samples and non-stoichiometry were examined by electron microprobe analysis (EMA). This showed that the oxides were well sintered, the distribution of the iron was homogeneous, all compositions were close to the nominal composition and the samples had no apparent interconnected pores. (tables 4.2-4, figs. 4.1-6)

<table>
<thead>
<tr>
<th>CaTi$_{1-x}$Fe$<em>x$O$</em>{3-\delta}$</th>
<th>SrTi$_{1-x}$Fe$<em>x$O$</em>{3-\delta}$</th>
<th>BaTi$_{1-x}$Fe$<em>x$O$</em>{3-\delta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>x</strong></td>
<td><strong>Synthesis conditions</strong></td>
<td><strong>x</strong></td>
</tr>
<tr>
<td>0.15</td>
<td>T=1300°C, 96 hours</td>
<td>0.15</td>
</tr>
<tr>
<td>0.3</td>
<td>T=1300°C, 72 hours</td>
<td>0.3</td>
</tr>
<tr>
<td>0.5</td>
<td>T=1200°C, 72 hours</td>
<td>0.5</td>
</tr>
<tr>
<td>0.8</td>
<td>T=1200°C, 72 hours</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table. 4.1. Synthesis conditions for CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$, SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ and BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ systems
4. SAMPLE PREPARATION AND CHARACTERIZATION

Fig. 4.1. Example of the x-ray powder diffraction pattern and Rietveld analysis for CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (x=0.15).

Fig. 4.2. Cell parameters for CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ as a function of iron content x. Black circles—present results, red squares—published data, Ref. [109]. The part of the minor scatter between present results and published data is most likely due to difference in $\delta$.

<table>
<thead>
<tr>
<th>x</th>
<th>Crystal structure and space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15(1)</td>
<td>Orth, Pnma</td>
</tr>
<tr>
<td>0.29(5)</td>
<td>Orth, Pnma</td>
</tr>
</tbody>
</table>

Table. 4.2. Results of microprobe analysis and XRD for CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system prepared in air.
4. SAMPLE PREPARATION AND CHARACTERIZATION

Crystal structure and space group

<table>
<thead>
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<th>x</th>
<th>Crystal structure and space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18(3)</td>
<td>Cubic, Pm3m</td>
</tr>
<tr>
<td>0.29(3)</td>
<td>Cubic, Pm3m</td>
</tr>
<tr>
<td>0.48(1)</td>
<td>Cubic, Pm3m</td>
</tr>
<tr>
<td>0.79(1)</td>
<td>Cubic, Pm3m</td>
</tr>
</tbody>
</table>

Table 4.3. Results of microprobe analysis and XRD for SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system prepared in air.

Fig. 4.3. Example of the x-ray powder diffraction pattern and Rietveld analysis for SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (x=0.15).

Fig. 4.4. Cell parameters for SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ as a function of iron content x. Black circles- present results, red squares- published data, Ref. [81]. The part of the minor scatter between present results and published data is most likely due to difference in $\delta$. 
4. SAMPLE PREPARATION AND CHARACTERIZATION

**Crystal structure and space group**

<table>
<thead>
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<th>x</th>
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</tr>
</thead>
<tbody>
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<td>0.12(3)</td>
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<td>0.20(1)</td>
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<td>0.31(5)</td>
<td>Hexagonal, P6\textsubscript{3}/mmc</td>
</tr>
<tr>
<td>0.62(4)</td>
<td>Hexagonal, P6\textsubscript{3}/mmc</td>
</tr>
</tbody>
</table>

Table 4.4. Results of microprobe analysis and XRD for BaTi\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3-δ} system prepared in air.

**Fig. 4.5.** Example of the x-ray powder diffraction pattern and Rietveld analysis for BaTi\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3-δ} (x=0.1)

**Fig. 4.6.** Cell parameters for BaTi\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3-δ} as a function of iron content x. Black circles- present results, red squares- published data, Ref. [87]. The part of the minor scatter between present results and published data is most likely due to difference in δ.
The BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$, CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$, SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ systems were investigated further for a characterization of their static (Mössbauer spectroscopy) and dynamical properties (quasielastic neutron scattering). For this reason the materials were heated for periods of 72 to 140 hours in open AgPd capsules at temperatures of 1200°C in CO-CO$_2$ gas mixtures corresponding to an oxygen fugacity of log$f$O$_2$=-11. Under these conditions, all iron in the samples is present as Fe$^{3+}$. Samples were drop quenched into the cool part of the furnace under flowing gas and examined again by x-ray diffraction and Mössbauer spectroscopy in order to prove the single phase and trivalent iron content.

- Magnetic structure of SrTi$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$

The structure of SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ with x= 0.8 was further investigated on the neutron diffractometer D20 at ILL with $\lambda$=1.30Å [96, 110]. The thermal evolution of the neutron powder diffraction patterns was acquired in the temperature range 23°C<T<1000°C. During the measurements the sample was exposed to a vacuum of about 10$^{-6}$mbar (at the pump inlet) corresponding to log$f$O$_2$=-6.6.

The sample of SrTi$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ was preliminarily treated under low oxygen fugacity and high temperature. Mössbauer spectra confirmed that all iron had an oxidation state 3+ and thus $\delta$=0.4

Diffraction data show evidence for magnetic ordering (fig. 4.7). Below 200°C, in addition to the structural Bragg peaks for the space group Pm3m new diffraction peaks appear both during the cooling and heating cycle ($2\theta \approx 17.5^0$, $33^0$ and $42^0$) which are attributed to magnetic superstructure peaks (fig. 4.7). This was also confirmed by Mössbauer spectroscopy, where spectra show long range magnetic ordering through a broad sextet.

The diffraction data on SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ with x=0.8 (T=109°C) were (partially) refined by the Rietveld method using the program Rietica. The magnetic part of the diffractogram was excluded and was treated as an additional phase. The magnetic diffraction pattern of the main phase was refined in the space group Pm3m with a random distribution of the Fe and Ti on B-sites. No extra peaks or additional splitting of the main cubic reflections were observed at T=109°C. Refinement with atoms at the ideal positions resulted in $R_p$=7.6%. Absorption of the cylindrical shaped sample holder had been taken into account (Table 4.5)
In the SrFeO<sub>x</sub> system, the oxygen concentration x can be varied within the range from 2.5 to 3. SrFeO<sub>2.5</sub> exhibits a transition from antiferromagnetism to paramagnetism at T<sub>N</sub>=693 K [79]. SrFeO<sub>3</sub> is a metallic conductor with helical magnetic ordering below 134 K [90]. The magnetic structure of these oxides is expected from the strong Fe-O-Fe exchange interaction [111, 112]. Obviously, substitution of another element at the Fe site changes the oxygen stoichiometry and thus the concentration of oxygen defects reduces the magnetic exchange interaction and induces the changes in the magnetic properties.

Deficiency of oxygen increases the Néel temperature (SrFeO<sub>2.5</sub>, T<sub>N</sub>=400°C) which is only T<sub>N</sub>=-139°C for a fully occupied oxygen lattice in SrFeO<sub>3</sub>. The oxide of the present interest with an intermediate concentration of oxygen defects shows an in-between temperature of about 200°C for the magnetic transition.

On the basis of literature data on magnetic ordering in perovskites one can choose the model of antiferromagnetic ordering. An antiferromagnetic structure is usually described by a single wave vector k. In our case the magnetic reflections can be indexed by the propagation vector k = (111) and antiferromagnetic interactions occur between atoms of the same spin (e.g. Fe<sup>3+</sup> and Fe<sup>3+</sup>). The strongest magnetic peak at 2θ = 17.5° corresponds to a d-spacing of 4.45 Å, exactly twice bigger than the ‘main’ structure peak at 2θ = 33.81°, d=2.23Å, hkl = (1 1 1) (fig. 4.8).
4. SAMPLE PREPARATION AND CHARACTERIZATION

Fig. 5.1.2.1. Thermal variation of the neutron powder diffraction patterns for the SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system with $x=0.8$. No background has been subtracted.

Fig. 5.1.2.2. The magnetic moments of the two iron atoms are oriented antiferromagnetically in the (111) plane. Magnetic interaction occurs between atoms of the same spin, e.g. Fe$^{3+}$ and Fe$^{3+}$. 
Chapter 5

Results

5.1. Static properties

5.1.1. A Mössbauer study of oxygen vacancy and cation distribution in 6H-BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$

The degree of non-stoichiometry in transition metal oxides is decisive for many properties. Despite the critical role of oxygen vacancies for the electrical conductivity, the arrangement of the defects in the structure has not been fully characterized yet.

For a first Mössbauer study of BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$, samples were synthesised over a range of compositions to investigate the cation distribution and short-range ordering of oxygen vacancies, and to discuss potential implications for the interpretation of conductivity data [113].

Results

The Mössbauer spectra of BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ consist of multiple overlapping doublets (fig. 5.1.1). The fitting approach took into account the structure of 6H-BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$, and the range of centre shifts observed for octahedral and pentahedral coordinated Fe$^{3+}$ in CaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ [75]. The validity of fits was judged on the basis of minimising the number of parameters and $\chi^2$ values, providing physically realistic fits to the spectra, and achieving consistency across the composition range. Conventional constraints were applied to the high- and low-velocity components of each doublet, i.e. equal area and equal width. The final fitting model consisted of one singlet assigned to octahedral Fe$^{3+}$, one doublet assigned to octahedral Fe$^{3+}$, and two doublets assigned to pentahedral Fe$^{2+}$. Hyperfine parameters are listed in table 5.1.1, where uncertainties are estimated based on statistical errors of the particular fitting model.

The presence of Fe$^{2+}$ was ruled out based on the absence of absorption at higher velocity (a centre shift of at least 1.0 mm/s relative to $\alpha$-Fe is expected lines, e.g. [97]) and the presence of Fe$^{4+}$ was ruled out based on the weighted mean centre shifts (a parameter which is relatively independent of the fitting model) which all fall within the range for Fe$^{3+}$. The absence of Fe$^{4+}$ is
consistent with previous work and the relatively reducing conditions used to synthesise the samples.

A minimum of two subspectra is required to fit octahedral $\text{Fe}^{3+}$ absorption in Mössbauer spectra of 6H- BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$, likely reflecting a distribution of $\text{Fe}^{3+}$ between the M1 and M2 sites. Most fitting trials with two octahedral $\text{Fe}^{3+}$ doublets of spectra from samples with low iron concentration returned zero for the quadrupole splitting of one of the doublets. Hence an octahedral $\text{Fe}^{3+}$ absorption as one doublet and one singlet were modelled. At low iron concentrations the singlet could be interpreted to indicate $\text{Fe}^{3+}$ in the M1 site (since it has cubic symmetry the quadrupole splitting should be zero), but the absence of the singlet in spectra from higher iron concentrations does not exclude the possibility of $\text{Fe}^{3+}$ occupying the M1 site. Symmetry could be lowered in the M1 site at higher iron concentrations (e.g. by next-nearest neighbour interactions) such that quadrupole splitting is no longer zero.

Hyperfine parameters for pentahedral $\text{Fe}^{3+}$ in BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ are similar to those for pentahedral $\text{Fe}^{3+}$ in CaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ [75]. One doublet was sufficient to model absorption assigned to pentahedral $\text{Fe}^{3+}$ in all BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ spectra except for $x=0.6$, where an additional doublet was required. In all fitting trials the centre shift of the two doublets in the $x=0.6$ spectrum assigned to pentahedral $\text{Fe}^{3+}$ were identical within experimental error, suggesting that the second doublet might correspond to a slightly different next-nearest neighbour environment. Such a difference could arise between pentahedral dimers occupied by Ti and $\text{Fe}^{3+}$, compared to those where $\text{Fe}^{3+}$ occupies both sites of the dimer. We consider it unlikely that the additional doublet could correspond to tetrahedral $\text{Fe}^{3+}$, since a significant difference in centre shift (greater than at least 0.02 mm/s) would be expected on removal of a coordinating oxygen.
### 5. RESULTS. STATIC PROPERTIES

Table 5.1.1. Hyperfine parameters for BaTi$_{1-x}$Fe$_x$O$_{3-2x/2}$ at 293 K

<table>
<thead>
<tr>
<th>Fe concentration ($x$)</th>
<th>0.1*</th>
<th>0.12(3)</th>
<th>0.20(2)</th>
<th>0.31(5)</th>
<th>0.62(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$^{57}$Fe$^{3+}$ doublet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>mm/s</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33(1)</td>
<td>0.34(1)</td>
</tr>
<tr>
<td>QS</td>
<td>mm/s</td>
<td>0.32(2)</td>
<td>0.43(8)</td>
<td>0.35(3)</td>
<td>0.38(2)</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>mm/s</td>
<td>0.41(4)</td>
<td>0.24(17)</td>
<td>0.28(6)</td>
<td>0.30(6)</td>
</tr>
<tr>
<td>area</td>
<td>%</td>
<td>35(20)</td>
<td>13(20)</td>
<td>33(13)</td>
<td>37(21)</td>
</tr>
<tr>
<td><strong>$^{57}$Fe$^{3+}$ singlet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>mm/s</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32(1)</td>
<td>0.33(1)</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>mm/s</td>
<td>0.40</td>
<td>0.38(18)</td>
<td>0.27(8)</td>
<td>0.25(20)</td>
</tr>
<tr>
<td>area</td>
<td>%</td>
<td>16(20)</td>
<td>34(28)</td>
<td>18(9)</td>
<td>8(8)</td>
</tr>
<tr>
<td><strong>$^{57}$Fe$^{3+}$ (I) doublet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>mm/s</td>
<td>0.29(2)</td>
<td>0.26(3)</td>
<td>0.27(1)</td>
<td>0.26(1)</td>
</tr>
<tr>
<td>QS</td>
<td>mm/s</td>
<td>0.67(2)</td>
<td>0.68(3)</td>
<td>0.71(2)</td>
<td>0.73(2)</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>mm/s</td>
<td>0.50</td>
<td>0.45(7)</td>
<td>0.37(2)</td>
<td>0.38(2)</td>
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<tr>
<td>area</td>
<td>%</td>
<td>49(20)</td>
<td>53(16)</td>
<td>49(5)</td>
<td>55(5)</td>
</tr>
<tr>
<td><strong>$^{57}$Fe$^{3+}$ (II) doublet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>mm/s</td>
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</tr>
<tr>
<td>QS</td>
<td>mm/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>mm/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>area</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes**

CS: centre shift (relative to $\alpha$-Fe); QS: quadrupole splitting; $\Gamma$: Lorentzian line width; area: relative area; VI, V, IV symbols corresponds to the octahedral, pentahedral and tetrahedral coordinated iron

Values in italics were held fixed during the fitting process

*nominal composition; synthesised with $^{57}$Fe
Discussion

In Mössbauer spectroscopy, the area of a subspectrum is related to the proportional abundance of iron on the corresponding crystallographic site, and to a first approximation the two can be considered equal. The relative area fractions listed in table 5.1.1 therefore give an indication of the relative abundance of Fe$^{3+}$ in the octahedral and pentahedral sites.

For samples of BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ containing only Fe$^{3+}$, and assuming that all Ti is present as Ti$^{4+}$, the number of oxygen vacancies can be calculated directly from the iron concentration based on electrostatic neutrality. Fig. 5.1.2. shows a comparison of this value with the one calculated from the Mössbauer data, based on one half oxygen vacancy per pentahedral site. The 1:1 correlation line indicates the variation expected if oxygen vacancies were only associated with Fe atoms. In this case each oxygen vacancy would be associated with two Fe atoms occupying both sites of an
M2-M2 pair, and no Fe would substitute onto the M1 site (fig. 5.1.3). One can rule out this possibility based on the systematic offset of the data from this line in fig. 5.1.2., and the degree to which the data deviate from the 1:1 correlation indicates the number of Ti atoms that are associated with oxygen vacancies.

One can calculate the number of oxygen vacancies associated with Fe and Ti based on a random distribution of cations over available sites. For samples with x<0.5, half of the pentahedral sites would be occupied by Fe$^{3+}$ and half would be occupied by Ti$^{4+}$. M2 dimers containing an oxygen vacancy are considered more likely to be Fe-Ti, rather than Ti-Ti or Fe-Fe. At higher iron concentrations, however, there are insufficient Ti atoms available to balance Fe; hence Fe-Fe pairs on the M2 site would become more common. This variation is indicated by the dotted line in fig. 5.1.2, where Fe is associated with 50% of the pentahedral sites up to x=0.5, but an
increasing fraction at higher iron concentrations. The dotted line appears to fit our Mössbauer data well, indicating that a random distribution of oxygen vacancies over O1 sites is consistent with our data.

The actual distribution of Fe and Ti over M1 and M2 cation sites is more difficult to determine. In principle the site distribution could be determined from the relative area data, but since the singlet and doublet assigned to octahedral Fe$^{3+}$ absorption overlap significantly, the errors would be extremely large. There is a possibility, however, to use the relative areas of pentahedral and octahedral subspectra to infer some qualitative aspects of the cation distribution over M1 and M2 sites. We consider two different cases where oxygen vacancies are randomly distributed over O1 sites as described above: (1) Fe and Ti are randomly distributed over M1 and M2 sites (dotted line in fig. 5.1.2); and (2) Fe substitutes on the M2 site only. At low iron concentrations, both cases would give a similar ratio for pentahedral to octahedral sites, since oxygen vacancies are also low in concentration. At higher iron concentrations, however, the chance of Fe-Fe pairs is significantly greater when Fe substitutes on the M2 site only, so that more oxygen vacancies are associated with Fe atoms. For an iron concentration of $x=0.6$, for example, the number of oxygen vacancies associated with Fe atoms for case (2) would be 0.27 per formula unit (p.f.u.), compared to 0.17 p.f.u. for case (1). It is clear that the latter value is more consistent with the Mössbauer data (fig. 5.1.2), and so we conclude that Fe does substitute on the M1 site, and that a random distribution of Fe and Ti atoms over the M1 and M2 sites is at least consistent with our data.

Mössbauer data do not support the presence of tetrahedral Fe$^{3+}$. This is in contrast to the results inferred from Rietveld refinements of 6H-BaTi$_{0.33}$Fe$_{0.67}$O$_{3-\delta}$ synthesised at significantly higher oxygen fugacities (in air and in flowing oxygen) [86]. A fraction of iron in the high vacancy sample ($\delta \approx 0.32$ based on weight loss) was inferred to be tetrahedrally coordinated based on differences in the $z$ positional parameter for the M2 site between neutron and X-ray data, where Fe and Ti could be distinguished in neutron data due to the opposite signs of their neutron scattering lengths. Comparison of these results with the present Mössbauer data suggests that the coordination of Fe$^{3+}$ (and hence the nature of oxygen vacancy ordering) may depend on Fe$^{4+}$/Fe$^{3+}$, since the result from measurement showed that samples with similar iron concentration synthesised in air always contained observable Fe$^{4+}$ (typically 1/3 of Fe) according to Mössbauer spectroscopy.

The distribution of oxygen vacancies in BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ provides insight into its conductivity. Ionic conductivity has been observed for samples in the concentration range $x=0.1$ to $x=0.5$ [83], although the magnitude is significantly less for equivalent compositions and temperatures
compared to CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ [114] and SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ [73]. One possible factor is a reduced mobility of oxygen ions in BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$, since oxygen vacancies are essentially constrained to two-dimensional movement along planes of O1 atoms. In contrast, oxygen vacancies can move in three dimensions at low iron concentrations within perovskite-structured SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ and CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$, e.g. [75]. On the other hand, ionic conductivity generally increases with increasing vacancy concentration in SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ and BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$, but decreases in CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ after reaching a maximum near x=0.2 [114]. This can be attributed to the ordering of oxygen vacancies in CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ into chains and eventually infinite planes, which dramatically reduces the mobility of vacancies [75]. In contrast, the lack of vacancy ordering in SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (x<0.8) and BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ leads to an enhancement of ionic conductivity with increasing concentration of oxygen vacancies. The presence of tetrahedral Fe$^{3+}$ in BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ [86], which implies short-range ordering of vacancies within planes of O1 atoms, would restrict the mobility of ionic charge carriers. There may be conditions, therefore, under which ionic conductivity is favoured compared to others, and a combined study incorporating Mössbauer spectroscopy and conductivity measurements could help to identify those conditions.
5. RESULTS. DYNAMIC PROPERTIES

5.2. Dynamic properties

5.2.1. Results on CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$

Electrical conductivity measurements allow access to the dynamical properties. Oxygen transport of mixed ionic-electronic conductors can be measured by a ‘relaxation’ technique. This permits investigation of the material dynamic properties which change with oxygen partial pressure. The oxygen chemical diffusion coefficient can be derived from such relaxation data. For materials exhibiting higher electronic than ionic conductivity, the time for a conductivity change is controlled by bulk ionic transport and surface reactions can be neglected.

The following chapter illustrates that ionic conductivity is independent of the oxygen fugacity, while the magnitude of the conductivity is given by the electronic transport properties. This statement is supported by investigations of CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$ using the conductivity relaxation technique.

The second part of the chapter describes a temperature dependent study of the dynamics of the anion vacancies over a wide temperature range, applying the neutron fixed window technique which is described in chapter 3. Experimental techniques. Quasielastic neutron scattering experiments have been carried out to study the thermally activated dynamics of oxygen vacancies. Due to the limited beam-time and the lack of the good statistics the spectra are treated by computer simulation based on the theoretical calculations.

Electrical conductivity

The temperature phase diagram of CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$ is shown in fig.5.2.1.1 by the red line.

Fig.5.2.1.1. Phase diagram of CaTi$_{1-x}$Fe$_{x}$O$_{3-\delta}$ system as a function of temperature and iron content. The bold vertical line indicates the composition of investigation [75].
5. RESULTS. DYNAMIC PROPERTIES

There is a structural phase transition at around 1150°C relating to the oxygen vacancies disorder in the oxygen sublattice. This is observed in our conductivity study by a pronounced hysteresis between the heating and cooling cycles (fig.5.2.1.2) taken at different heating/cooling rates by heating the sample between 900°C and 1250°C. Also, this is a good demonstration of largely different conductivities which depend on the thermal history of the sample. The width of the hysteresis region depends on the rate of temperature change and becomes narrower for the slower rate. At the cooling regime the conductivity drops very significantly with a cooling rate reflecting a closer approach to equilibrium and reflecting the kinetics of the ordering reaction. As the order-disorder reaction is rather slow, all ramps show a hysteresis in the conductivity and the transition temperature is shifted to lower temperatures due to supercooling effects.

![Fig. 5.2.1.2. Electrical conductivity measured as a function of temperature at different heating-cooling rates](image)

The kinetics involves mass transport with the formation of microdomains observed directly by TEM [72, 75, 76]. It must be assured that conductivity values represent for equilibrium conditions. This can be checked by following the time evolution of relaxation curves e.g. after a change in temperature or in oxygen pressure. Conductivity relaxation experiments have been conducted on CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$ samples by abruptly changing the oxygen partial pressure and monitoring the change of the conductivity as a function of time.
5. RESULTS. DYNAMIC PROPERTIES

- Equilibrium electrical conductivity

Fig.5.2.1.3 shows the equilibrium electrical conductivity as measured against oxygen partial pressure at different temperatures. The total conductivity increases with increasing temperature.

One can see that the smooth dependence of the total conductivity on oxygen pressure, characteristic for many mixed oxide conductors exhibiting both p- and n-type electronic conduction (section 1.4.2. Total electrical conductivity of a mixed conductor), is observed for CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$. At low oxygen partial pressure $\log \sigma$ tends towards $-\frac{1}{4}$ when plotted against $\log P_{O_2}$. This is in perfect agreement with earlier reports [11, 114].

At intermediate $P_{O_2}$ the conductivity curves show a flat region, assigned to ionic conductivity, which is due to oxygen vacancies and which is expected to be independent of $P_{O_2}$. The ionic conductivity increases with temperature in a nonlinear manner, which is indicative for a structural phase transition due to the ordering of oxygen vacancies (fig.5.2.1.4).

Under these conditions of temperature and oxygen partial pressure CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$ is an ideal material for the conductivity relaxation technique. The electronic conductivity of CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$ is several orders of magnitude larger than the ionic conductivity and so the relaxation profiles measured using conductivity relaxation is primarily due to the transport of ionic species.

Fig.5.2.1.3. Equilibrium, total electrical conductivity vs. oxygen partial pressure at different temperatures.

Fig. 5.2.1.4. Ionic conductivity of CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$. The dotted line is a schematic guide to the eye, based on the phase equilibrium data shown in fig. 5.2.1.1.
5. RESULTS. DYNAMIC PROPERTIES

- Conductivity relaxation kinetics

The change of $P_{O_2}$ and electrical conductivity during an isothermal re-equilibration experiment, involving oxidation and reduction, is shown together with the fitting curves in fig. 5.2.1.5. As seen, a sudden imposition of an increased/decreased oxygen activity results in a responsive change of electrical conductivity from the initial value, $\sigma(0)$, to the final value, $\sigma(\infty)$ (eq. 1.4.4.12). The conductivity initially exhibits rapid changes and then approaches asymptotically the final value which may be considered as an equilibrium state. Data show a reached equilibrium when setting different fugacities in reverse order. The time constants for the oxidizing and the reducing process are nearly equal and thus independent of the switch direction.

![Fig. 5.2.1.5. Isothermal changes of the electrical conductivity during oxidation and reduction runs at T=1200°C.](image)

As it was shown in section 1.4.4 Oxygen self-diffusion coefficient the conductivity changes with time according to Eq. (1.4.4.12) and a mean square fit gives the diffusion coefficient. Here a new model for the data interpretation is proposed.

Conductivity relaxation data were analyzed by least-squares fitting to equation:

$$y = y_0 + A \exp(t/\tau),$$

(5.2.1.1)

where $y_0$ is the equilibrated conductivity value, $A$ is an amplitude factor and $\tau$ is the relaxation constant. The above solution of the diffusion equation is valid under the assumption that only
one type of defects is responsible for the equilibration kinetics within the entire equilibration range.

It is essential to consider the effects of the sample dimensions on the equilibration kinetics and the related changes of the electrical conductivity for the equilibrium mechanism. As seen from Eq. (1.4.4.12) a thicker sample will lead to a longer relaxation constant. In the present case, a description with a simple exponential function represents a first order approximation for a rectangular shaped sample geometry (3.0×4.6×11.2 mm for CaTi$_{0.7}$Fe$_{0.3}$O$_{3-δ}$). An appropriate time behavior for this shape is given by an infinite sum of exponentials where the individual decay times and amplitudes are related by numerical factors Eq. (1.4.4.12) [26]. Thus the number of free parameters is not increased. The computer simulation in fig.5.2.1.6 shows the significance of the higher order terms for the short time region.

According to the section 3.6. Experimental techniques. Electrical conductivity, the first 260 seconds are excluded from the data treatment due to the time needed for oxygen delivery to the setup. For longer times, the data have been evaluated by the first order approximation which is well suited to extract the equilibrium conductivity.

![Fig. 5.2.1.6. An example of a fit of a relaxation curve including high order terms.](image)

Two typical conductivity spectra are shown on fig. 5.2.1.7, together with the fitting results, using $τ$, $y_0$ and $A$ from eq. 5.2.1.1 as the adjustable parameter. The agreement between experimental data and the theoretical curves are very good.
5. RESULTS. DYNAMIC PROPERTIES

Discussion

An inspection of the relaxation times for a given temperature shows that they are independent of the oxygen fugacity, whereas the total conductivity varies up to a factor of 3. The fitted values are 850±24, 475±4 and 62±2 seconds for T=1000°C, T=1100°C and T=1200°C. It appears that the electronic contribution is dominating in the present fugacity range as indicated by the slope of -1/4 in fig. 5.2.1.3. Electronic processes adjust fast on the time scale of the present experiments. However the electronic conductivity can only adopt its equilibrium value according to the change of the local oxygen stoichiometry. Thus the ionic conductivity is the rate determining process at all fugacities, while the magnitude of the conductivity is given by the electronic transport properties. In consequence the time constants can be evaluated to provide the diffusion constants and thus the ionic conductivity at any value of oxygen fugacity.

The time constants relate to the chemical diffusion constants as shown by J. Crank [26]. From the first order fits of the relaxation spectra one can obtain the chemical diffusion coefficient. The corresponding ionic conductivities are evaluated from diffusion constants through the Nernst-Einstein relation (table 5.2.1.1).

<table>
<thead>
<tr>
<th>T, °C</th>
<th>( \tau ), seconds</th>
<th>( D_{\text{chem.}} ), cm(^2)/s</th>
<th>( \sigma_{\text{ion.}} ), S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>62±2</td>
<td>((1.71±0.03)\times10^{-5})</td>
<td>0.231±0.004</td>
</tr>
<tr>
<td>1100</td>
<td>475±4</td>
<td>((2.13±0.02)\times10^{-6})</td>
<td>0.031±0.0003</td>
</tr>
<tr>
<td>1000</td>
<td>850±24</td>
<td>((1.22±0.04)\times10^{-6})</td>
<td>0.019±0.0005</td>
</tr>
</tbody>
</table>

Table. 5.2.1.1. \( D_{\text{chem.}} \) and \( \sigma_{\text{ion.}} \) evaluated from conductivity relaxation experiments
Measured equilibrated values of electrical conductivity are shown on fig.5.2.1.8 together with the levels of ionic conductivity calculated from relaxation measurements (dashed lines). The good fit in the regions where the total conductivity is constant indicates that the region of ionic dominance has been approached.

The ionic conductivity has been extracted from the observed relaxation times independent of the fugacity setting. These values correspond to the ionic conductivity extracted in the traditional way from the minimum of the total conductivity at intermediate fugacity values. The observed agreement between the ionic conductivities obtained at low $P_{O_2}$ by the relaxation technique and those monitored by direct measurements of ionic conductivity suggests that the equilibration kinetics are determined by the transport of oxygen vacancies only.

**Neutron study**

Directly measured values of ionic conductivity and calculated from relaxation experiments for CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ $\sigma_{\text{ion}} = 0.019, 0.031$ and $0.231$ S/cm at $1000^\circ$C, $1100^\circ$C and $1200^\circ$C correspond to quasielastic line widths of about 20, 35 and 286 $\mu$eV respectively (translational diffusion model for $Q=1\text{Å}^{-1}$). Based on these estimates quasielastic measurements have been performed on the backscattering spectrometer IN10 with $1\mu$eV resolution [115], which is appropriate to study diffusion constants in the range of $10^{-6}$ to $10^{-8}$ cm$^2$/s.
1. Fixed window scans

Further, this instrument allows a search with high efficiency for temperature anomalies of the scattered intensity in a particular run mode, called fixed window scans where the truly elastic intensity (within the energy resolution of 1 μeV) is analyzed. Diffusion may be observable in regions with an anomalous behavior of the elastic intensity. Fixed window scans were taken with the sample temperature varying between room temperature and 1400°C. A high temperature furnace operating at a high vacuum served as the sample environment for the measurements. Temperature was controlled via two S type thermocouples. Absolute temperature accuracy is estimated to ±3°C. Parts of analysers which correspond to the Bragg angles of the sample and its container were screened using cadmium sheets to prevent the spectra from being spoiled by intense elastic scattering.

Results from IN10 are shown in fig. 5.2.1.9. The data reveal intensity steps at 770°C and 920°C. In analogy to [72, 75, 76] one can attribute the intensity steps observed to structural phase transitions. An intensity reduction is due to the Debye-Waller factor and oxygen diffusion. A further anomaly appears around 1100°C in particular for Q=1.7 Å\(^{-1}\) (circled area in fig. 5.2.1.9). Closer inspection reveals a pronounced hysteresis in the count rate between the heating and cooling cycle.

A similar feature was obtained on HFBS (1μeV resolution); however at much smaller Q values of 0.25 Å\(^{-1}\) and 0.37 Å\(^{-1}\) (fig. 5.2.1.10) not accessible for measurements on IN10. We assume that the order – disorder transition in the oxygen sublattice referred to above is the origin of this anomaly [72, 75, 76]. The hysteresis loop suggests that the transition is of first order. It is emphasized that hysteresis loops are observed in two distinct Q-regimes and thus provide information on two different length scales which are 3.7 Å for IN10 and a range from 17 Å to 25 Å for HFBS. We attribute the shorter length scale to the correlation length between the ordered defects while the longer length scale is characteristic for the formation of micro-domains. The Q-resolution on backscattering instruments is relaxed to ± 0.05 Å\(^{-1}\) to ± 0.1 Å\(^{-1}\) depending on scattering angle and instrumental settings and hence the above lengths may have uncertainties of 5 to 15 %. 
Fig 5.2.1.9. Fixed window scans from IN10 for CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$. The space group assignment has been made according to Ref. [72, 75, 76]. The circled area indicates a region of an intensity anomaly due to the order and disorder transition in the arrangements of defects on the oxygen sublattice.
2. Quasielastic neutron scattering

- Calculation of cross-sections

The individual scattering cross sections were calculated within the model describing the oxygen induced diffusion for CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$ (table 5.2.1.1). $\sigma_{\text{coh}}$ considers the contributions from all elements in the unit cell including the coherent part of the oxygen (eq. 1.5.6.1-4). However, this intensity in a perfect structure is concentrated in the Bragg peaks (and in phonon contributions) which are of no relevance here. Similar, $\sigma_{\text{inc}}$ adds the contributions from all atomic species including the Laue term from the oxygen defects. This later term is given separately in column 4 of table 5.2.1.2. Discarding the $Q$-regions with Bragg scattering, the part of the signal which one expects to become quasielastically broadened is given by $\sigma_{\text{inc}}^{\text{defects}}$. This quasielastic fraction compared to the total incoherent scattering is given in column 6:

<table>
<thead>
<tr>
<th>composition</th>
<th>$\sigma_{\text{coh}}$, barns</th>
<th>$\sigma_{\text{inc}}$, barns</th>
<th>$\sigma_{\text{inc}}^{\text{defects}}$, barns</th>
<th>$\sigma_{\text{abs}}$, barns</th>
<th>$\sigma_{\text{inc}}/\sigma_{\text{inc}}^{\text{defects}}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.3</td>
<td>6.88</td>
<td>6.57</td>
<td>0.20</td>
<td>19.05</td>
<td>3.10</td>
</tr>
</tbody>
</table>

Table 5.2.1.2. Calculated cross-sections for the CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$

* The absorption cross-section was calculated for the neutron energy corresponding to the IN10 backscattering instrument (E=2.08 meV).

Quasielastic scans have been performed at T=800°C (frozen dynamics) and at T=1135°C (midpoint of the intensity drop) in order to look for the oxygen dynamics (fig. 5.2.1.11a). The scan range was +/- 6 μeV. The resolution function is shown by the black line. The high temperature data described by a red/grey line indicates additional intensity in the near-wings of
the resolution function. Such a pattern is expected from diffusing oxygen. Because the statistics are not good enough to allow for an unambiguous quasielastic fit, a simulation is shown in fig. 5.2.1.11b. The resolution function is approximated by a Gaussian profile, shown as a black line. A Lorentzian profile (not convoluted) to simulate a quasielastic signal with a height of 3% according to the calculations (table 5.2.1.2) for CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$ is shown by the red/grey line. A resembling description is obtained for a quasielastic component with a FWHM of 3 $\mu$eV which corresponds to a diffusion coefficient of $D=7.8 \times 10^{-8}$ cm$^2$/s. This diffusion constant is significantly lower than the one derived from dc-conductivity measurements. One can assume that the type of diffusion is not a translation but local rotation. Due to the very modest statistics of these QENS data and because of a missing Q-dependence one can not definitely determine the true motion for this compound.

Fig. 5.2.1.11. a) Quasielastic spectrum for CaTi$_{0.7}$Fe$_{0.3}$O$_{3-\delta}$ at $= 1.7$ Å$^{-1}$. Open circles: 1135°C, filled circles: 800°C. Data are normalized to monitor. The following lines are guides to the eye: black describes the resolution function (800°C), red/grey represents data at 1135°C.

b) A simulation of spectra: black line represents a Gaussian resolution function (FWHM 1$\mu$eV), red/grey line is a Lorentzian component with an amplitude of 3% as expected for CaTi$_{0.7}$Fe$_{0.3}$O$_{2.85}$. 
5. RESULTS. DYNAMIC PROPERTIES

5.2.2 Results on SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system

This section consists of two parts. One describes the macroscopic diffusion measured by electrical conductivity and the second part deals with microscopic diffusion observed by quasielastic neutron scattering.

Strontium titanate doped with iron is a promising material for resistive high temperature oxygen sensors. However, a disadvantage of this and of many other metal oxides is the strong temperature dependence of conductivity. In the first part of this section it is shown that the temperature dependence of SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ can be adjusted by the iron content.

The experimental study of the dynamics on a microscopic scale is fundamental for an understanding of the interaction between anions and the lattice environment. In the second part of this section the results of high-resolution quasielastic experiments together with direct geometry time of flight data are presented. The analysis of the quasielastic linewidths, determined as a function of both momentum transfer and temperature reveals a new picture of the anion local motion. Geometric models for the oxygen rotational diffusion are proposed.

**Electrical conductivity**

The electrical conductivity of the SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ ($x=0-0.8$) system is investigated by measurements of the conductivity over a broad range of oxygen activities and temperatures (fig.5.2.2.1). The measurements were carried out in the mode of decreasing oxygen partial pressure in isothermal runs. It should be noted that the overall time necessary for carrying out measurements for one specimen takes about 200-250h.

In the low $P_{O_2}$ region, the curves of log conductivity show a $-\frac{1}{4}$ slope, attributed to n-type conductivity. At intermediate $P_{O_2}$ the conductivity curves show the beginning of the flat region. It is assigned to an ionic conductivity contribution due to the oxygen vacancies and it is independent of $P_{O_2}$ (section 1.4.2 Total electrical conductivity of a mixed conductor). At the same time, these results and those of others [73, 81] are in a good correspondence.

The ionic conductivity increases with increasing iron content (fig. 5.2.2.2). The $\sigma(x)$ increase follows the oxygen vacancy increase. One can suppose, therefore, that the average oxidation state of iron is 3+ or, in other words, the composition of the oxide remains close to SrTi$_{1-x}$Fe$_x$O$_{3-\delta/2}$. This reasonable supposition corresponds to the primary ionic compensation of acceptors. The shape of the curves reflects changes in ionic conductivity with acceptor...
concentration in the perovskite lattice having \( x/2 \) random vacancies and \((3-x/2)\) regular oxygen ions per elementary unit. Those results are in a good agreement with the \( c(c-1) \) dependence described in section 1.4.3 Ionic conductivity (fig. 1.4.3).

The ionic conductivity of different compositions in the temperature range of \( 900^\circ\text{C} < T < 1200^\circ\text{C} \) is plotted in fig. 5.2.2.3 as a function of the reciprocal temperature. A good linear dependence of \( \log(\sigma_{\text{ionic}}T) \) on the reciprocal absolute temperature is observed indicating no structural phase transitions due to ordering of oxygen vacancies. The activation energy \( E_{\text{act}} \) can be estimated from the slopes of the curves and the values are given below:

<table>
<thead>
<tr>
<th>x</th>
<th>0.15</th>
<th>0.3</th>
<th>0.5</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{act}} ) ±0.01, eV</td>
<td>0.79</td>
<td>0.85</td>
<td>0.85</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 5.2.2.1. The activation energies of the ionic contribution.

\( E_{\text{act}} \) increases with increasing iron content. At the same time the level of ionic conductivity increases with iron content too.

Fig. 5.2.2.1 Total conductivities for compositions in the system \( \text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \)
5. RESULTS. DYNAMIC PROPERTIES

Fig. 5.2.2.2. The ionic conductivity vs. iron concentration in SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$.

Neutron experiments

1. Fixed window scans
   - Calculation of cross-sections

The individual scattering cross sections were calculated as described in section 1.5.6. Oxygen induced diffusion. The quasielastic fraction compared to the total incoherent scattering and given in column 6 varies with composition, but it remains small under all conditions. This stems largely from the fact that titanium has a high incoherent cross section of 2.67 barns.

<table>
<thead>
<tr>
<th>composition</th>
<th>$\sigma_{\text{coh}}$, barns</th>
<th>$\sigma_{\text{inc}}$, barns</th>
<th>$\sigma_{\text{inc}}^{\text{defects}}$, barns</th>
<th>$\sigma_{\text{abs}}$, barns</th>
<th>$\sigma_{\text{inc}}/\sigma_{\text{inc}}^{\text{defects}}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.3</td>
<td>10.049</td>
<td>6.577</td>
<td>0.201</td>
<td>22.011</td>
<td>3.1</td>
</tr>
<tr>
<td>x=0.5</td>
<td>10.971</td>
<td>7.073</td>
<td>0.323</td>
<td>19.548</td>
<td>4.6</td>
</tr>
<tr>
<td>x=0.8</td>
<td>15.479</td>
<td>4.690</td>
<td>0.489</td>
<td>15.855</td>
<td>10.4</td>
</tr>
</tbody>
</table>

Table 5.2.2.2. Calculated cross-sections for SrTi$_{1-x}$Fe$_x$O$_{3-x/2}$ (x=0.3, 0.5, 0.8).

* The absorption cross-section was calculated for the neutron energy corresponding to the IN10 backscattering instrument (E=2.08 meV)

Fixed window temperature scans in SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (x=0.3, 0.5, 0.8) were carried out at IN16 (ILL) and HFBS (NIST) instruments to define appropriate temperature regimes for the observation of oxygen diffusion and to perform later energy-resolved quasielastic scans (fig. 5.2.2.4). The HFBS instrument has a higher count rate by about a factor of 7. This can shorten
5. RESULTS. DYNAMIC PROPERTIES

significantly the time of the experiment. The experiment conditions are described in section 5.2.1. Results on CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ Neutron study.

Hysteresis for the heating/cooling cycles for SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ x=0.8 at low temperatures (<200°C) may be due to the magnetic transition described earlier (chapter 4. Sample preparation and characterization).

Measured inelastic intensities show an obvious intensity step for all compositions within the $Q$ range from 0.56 Å$^{-1}$ to 1.78 Å$^{-1}$, an example for $Q$=1.22 Å is shown in fig. 5.2.2.4. The temperature window where the step is found becomes more narrow with the iron increase. This means that the oxygen diffusion is a function of defect concentration and in particular the activation energy increases with $x$. In addition, the intensity step is shifted to lower temperatures with increasing iron content. This implies that the oxygen diffusion becomes faster for higher doping. This has been clearly confirmed by the electrical conductivity data (fig. 5.2.2.2).

The contribution of the oxygen vacancies to the incoherent scattering is calculated at every measured $Q$ value (table 5.2.2.3) and compared to the theoretical predicted values (table 5.2.2.2, column 6). A slight discrepancy could be due to the possible contribution of different types of oxygen mobility (rotational and translational components) to the quasielastic line leading to a reduction of the intensity of the elastic line.

Table 5.2.2.3. Measured intensity changes which correspond to the contribution of the oxygen diffusion to the total incoherent scattering.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Intensity change, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>4.68</td>
</tr>
<tr>
<td>0.5</td>
<td>9.66</td>
</tr>
<tr>
<td>0.8</td>
<td>25.85</td>
</tr>
</tbody>
</table>

Fig. 5.2.2.4. Example of the fixed window scan for SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (x=0.3, 0.5, 0.8) at Q=1.22 Å. Shaded regions correspond to the intensity steps indicating a temperature window for the oxygen diffusion which can be observed at the instrument with 1µeV resolution. Red and blue lines correspond to heating and cooling regimes, respectively.
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2. Quasielastic neutron scattering

\textit{SrTi}_{0.5}\textit{Fe}_{0.5}\textit{O}_{3-\delta}

Energy resolved scans have been taken at instrument IN16 [116] at 380°C, 420°C and 480°C as the starting, intermediate and final temperatures of the intensity step for \textit{SrTi}_{1-x}\textit{Fe}_{x}\textit{O}_{3-\delta} (x=0.5). Typical counting times per temperature have been 10 hours. The Si(111) reflections have been used for monochromatising the incident beam and analyzing the scattering neutron wavelength. Runs with a vanadium sample (which is an entirely incoherent scatterer) were performed to obtain data for the normalization of the spectra and for the determination of the elastic energy resolution. The densely packed sample had a rectangular shape and was placed at an angle of 45° to the incoming beam. Only the scattering intensity through the sample was measured. Parts of the analyser crystals which correspond to the Bragg angles were screened with cadmium shields.

The data were normalized and corrected for self absorption and detector efficiency using the standard program packages for data analyses available at the spectrometer.

The corrected data have been fitted using a single Lorentzian to present the quasielastic intensity. An example of the quasielastic broadening is shown on fig. 5.2.2.5. The resulting line widths are given in fig. 5.2.2.6 as a function of momentum transfer. The Q dependence can be interpreted as the traits of a rotational jump diffusion which appears to be independent of the scattering vector within the error bars.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.2.2.5}
\caption{Energy resolved scan for \textit{SrTi}_{1-x}\textit{Fe}_{x}\textit{O}_{3-\delta} (x=0.5) at Q=1.78 Å, T=480°C.}
\end{figure}
5. RESULTS. DYNAMIC PROPERTIES

Discussion

The quasielastic spectral functions broaden with increasing temperature. The temperature dependence can be described by an Arrhenius law:

$$\Gamma = \Gamma_0 \exp\left(\frac{E_{\text{act}}}{RT}\right),$$

(5.2.2.1)

where $E_{\text{act}}$ is the activation energy, related to the height of the potential barrier hindering the rotational motion and $\Gamma$ is the width of the Lorentzian function. Also, the activation energy can be estimated from electrical conductivity data which has been taken at the same temperature and oxygen fugacity conditions as a neutron experiment (fig. 5.2.2.7), e.g. $300^\circ\text{C} < T < 500^\circ\text{C}$ and $\log P_{\text{O}_2} = -10$.

From Arrhenius plots activation energies of $0.27 \pm 0.11$ eV and $0.74 \pm 0.01$ eV were calculated for the neutron and for the conductivity experiments, respectively. The large difference in the
activation energies is interpreted by the fact that two different type of motion are observed. In the neutron case and using the approximation of small amplitudes of oscillations [117], one obtains with the help of the Arrhenius law the expression for rotational diffusion:

\[ \frac{h}{(\Gamma/2)} = \tau = \tau_0 \exp(\frac{E_{\text{act.}}}{kT}) , \] (5.2.2.2)

where \( \tau \) is the average time between two successive jumps and \( \tau_0 \) is a pre-exponential factor. The rotational diffusion coefficient is \( D = l^2 / 6\tau \) assuming that oxygen can rotate with the same probability between equivalent sites at the distance \( l \). In table 5.2.2.4 neutron data are compared with data obtained from electrical conductivity.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Conductivity</th>
<th>Neutrons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D \times 10^{-8}, , \text{cm}^2/\text{s} )</td>
<td>( \tau \times 10^{-9}, , \text{sec} )</td>
</tr>
<tr>
<td>380</td>
<td>1.8</td>
<td>3.5</td>
</tr>
<tr>
<td>420</td>
<td>4.2</td>
<td>1.5</td>
</tr>
<tr>
<td>480</td>
<td>8.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table. 5.2.2.4. Diffusion parameters observed by electrical conductivity and QENS measurements

One can note that the diffusion coefficient \( D \) from neutron data is lower and the average time \( \tau \) between jumps is shorter than for data calculated from electrical conductivity. This can be explained from a simple model outlined in fig. 5.2.2.8. When the oxygen rotates within the octahedron, its potential barrier is lower than for oxygen jumping to the next ‘free’ site of the neighbouring octahedron in the unit cell. Also note that the oxygen rotation does not contribute to charge transfer and is undetectable in the electrical conductivity measurements. Thus, for the first time the oxygen rotation is detected and the activation energy for this mode is measured.
Fig. 5.2.2.8. The energetic potential for the two sites model describing the neutron and electrical conductivity data. The small barrier (0.27eV) corresponds to rotational diffusion and has shorter jump time ($\tau_1$) and shorter distance than the motion determined by the higher potential barrier (0.74eV) which corresponds to translational diffusion and has a longer jump distance and longer dwell time ($\tau_2$).
In this section the results from computer simulations and model calculations for ion dynamics are presented and compared with experimental findings in several quasielastic neutron scattering experiments on SrTi$_{0.2}$Fe$_{0.8}$O$_{3.6}$.

QENS spectra were obtained in the ToF spectrometer IN5 and high resolution results were collected on the backscattering spectrometer IN16, both at the Institute Laue-Langevin in Grenoble. In all cases, the compact powder sample was contained in a platinum container (low absorption coefficient) which had a cylindrical shape in order to reduce the multiple scattering. The raw data were calibrated in a separate measuring run with a plate made from the incoherent scatterer vanadium. The experimental background was measured with the empty Pt container at room temperature. The background includes the contribution in the raw sample data from the furnace and the sample container. Both were also subtracted from the raw data. The detectors were grouped in order to improve the counting statistics. \( Q \) ranges exhibiting Bragg peaks have been excluded from further analysis.

- Backscattering

QENS spectra for SrTi$_{0.2}$Fe$_{0.8}$O$_{3.6}$ were collected at 420°C, 600°C and 700°C on instrument IN16 [118]. Data were fitted with a sum of \( \delta \)-functions and a single Lorenzian both convoluted with the instrumental resolution function.

The line width of the quasielastic signal is plotted as a function of the momentum transfer in fig. 5.2.2.9. Zero line widths means that no quasielastic contribution to the total incoherent scattering was detectable. The Lorentzian linewidth representing the quasielastic contribution shows no strong dependence on the scattering vector \( Q \), indicating that the broadening is caused by a localized motion.

The quasielastic line width increases with temperature in an Arrhenius-type fashion, the activation energy being $0.33\pm0.03$eV (fig. 5.2.2.10)
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ToF experiments

The composition SrTi$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ was further investigated in a regime of characteristic times of between $10^{-6}$ to $10^{-13}$ s, by time-of-flight spectroscopy. Typical energy transfers measured by time-of-flight methods are $10^{-5}$ to $10^{-2}$ eV.

A first experiment was performed on the IN5 chopper spectrometer at the ILL using incident wavelengths of 5.5 Å and 10.5 Å with resolution widths of the elastic peak of 70 µeV and 15 µeV, respectively (table 5.2.2.5). The resolution width and energy window depend on incident wavelength in opposite ways (section 3.2. Dynamic properties. QENS). Thus, the use of two sets of measurement allows more extensive study of the quasielastic broadening due to the oxygen diffusion.

<table>
<thead>
<tr>
<th>$\lambda_0$, Å / $\Delta E$, µeV</th>
<th>Q, Å$^{-1}$</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5 Å 70 µeV</td>
<td>0.45&lt;Q&lt;2.03</td>
<td>800°C, 900°C, 1000°C, 1200°C, 1350°C</td>
</tr>
<tr>
<td>10.5 Å 15 µeV</td>
<td>0.24&lt;Q&lt;1.05</td>
<td>700°C, 800°C, 1000°C</td>
</tr>
</tbody>
</table>

Table. 5.2.2.5. Instrument and experimental conditions of the neutron scattering experiment. $\lambda_0$ is the wavelength of the incident neutrons, $\Delta E$ is the full width at half maximum of the resolution function, and Q is the momentum transfer range for the elastic scattering.
All measured spectra contain strong contributions from collective lattice vibration (phonons) (fig. 5.2.2.11). However they are located at sufficiently high energy transfer such that there is no asymmetric broadening of the quasielastic peak. As a consequence the influence of the phonon scattering was neglected.

The elastic part of the incoherent scattering becomes reduced with increasing temperature, maybe for two reasons: (1) part has become quasielastic, (2) part has become inelastic (phonon scattering).

![Graph showing measured spectra with strong phonon contribution at high energy transfer.](image1)

![Graph showing corrected spectra at 1000°C and 800°C.](image2)

All samples show the presence of the quasi elastic broadening. Some low-resolution data (i.e., shorter wavelength) are influenced by Bragg scattering at high $Q$. They were easily removed from the data set. Data were fitted with a sum of resolution functions ($\delta$-function) and a single Lorenzian (representing the quasielastic scattering from oxygen). Fig. 5.2.2.12. shows an example of corrected spectra at 1000°C and 800°C for both incident wavelengths.
5. RESULTS. DYNAMIC PROPERTIES

The Lorentzian line width for both resolutions and for all temperatures does not depend on Q, indicating the localized character of the observed rotation motion (fig. 5.2.2.13).

Fig. 5.2.2.12. An example of the quasielastic spectra measured at Q=0.86 Å⁻¹ at different temperatures and different incident wavelengths. Green line- resolution function, blue line- quasielastic component, red line-resulting fit.

The Lorentzian line width for both resolutions and for all temperatures does not depend on Q, indicating the localized character of the observed rotation motion (fig. 5.2.2.13).

Fig. 5.2.2.13. An example of the Q-dependence of the quasielastic line width for both resolutions shown at 800°C and 1000°C. The FWHMs are independent of the scattering angle.
The low resolution data show a broader FWHM for the Lorentzian than the high resolution data at all measured temperatures. This indicates two different types of local motions, a fast one measured with 5.5Å and a slow one measured with 10.5Å. The following discussion will be concentrated on these two temperatures (800°C and 1000°C) measured at two different resolutions.

The quasielastic line widths observed with the two different instrument settings increase with temperature, and plotting them logarithmically against the inverse temperature indicates that they are thermally-activated with activation energies of $0.43\pm0.06 \text{ eV}$ and $0.27\pm0.02 \text{ eV}$ for incident wave length 10.5Å and 5.5 Å, respectively (fig. 5.2.2.14).

![Arrhenius plot for the quasielastic neutron scattering linewidth measured at 5.5Å and 10.5 Å incident wave lengths.](image)

**Discussion**

*Elastic incoherent structure factor*

The characteristic features of the neutron scattering results confirm that the monitored diffusion is a rotation or a local motion. Decisions between alternative models are usually made on the basis of the elastic incoherent structure factor. The EISF is the fraction of the total incoherent intensity which is contained in the purely elastic peak. Different modes of local motion can be distinguished by examining the $Q$-dependent intensity of the EISF.

Experimental results from IN16 and IN5 are shown in fig. 5.2.2.15-17 for all temperatures. The data show no trend for a change of the intensities with temperature for $Q<1.5\text{Å}^{-1}$, indicating that the mechanism of the underlying motion does not change.
5. RESULTS. DYNAMIC PROPERTIES

The total scattering function is a sum of elastic and inelastic contributions (section 1.5.4, Elastic and quasielastic scattering). Assuming two types of local motions (fig. 5.2.2.13.) one can express \( S(Q, \omega) \) in the following form, keeping in mind that an integration of the incoherent scattering contribution over energy is unity (eq. 1.5.3.7):
5. RESULTS. DYNAMIC PROPERTIES

\[ S(Q, \omega) = \delta A_i(Q) + L_i(1 - A_i(Q)) + \delta A_s(Q) + L_s(1 - A_s(Q)) = \]
\[ = \delta \left( A_i(Q) + A_s(Q) \right) + L_i(1 - A_i(Q)) + L_s(1 - A_s(Q)) \]  

(5.2.2.1)

where indexes 1 and 2 correspond to the different wave lengths, and I and II represent scattering from two types of motions. Thus, the scattering function consists of two components. One does not depend on initial wavelength \( \lambda_0 \), i.e. instrument resolution (elastic incoherent component) whereas the second depends on \( \lambda_0 \) (quasielastic component) (fig. 5.2.2.15-17, 5.2.2.22 ). Based on these assumptions one can estimate the geometry of the local motion and number of crystallographic sites involved in these motions (section 1.5.5. Diffusive scattering. Rotational diffusion)

- Short range diffuse scattering

At high Q-values the intensity of the quasielastic contribution rises monotonically with Q indicating a coherent contribution. Due to vibrations of the scatterers which weaken both elastic and inelastic parts of the scattering function, the intensities at high Q are reduced by a Debye-Waller factor and a clear temperature dependence is observed. In the following a possible interpretation of the coherent quasielastic contribution is given. However, no quantitative analysis is presented because the coherent scattering is outside the topic of the study.

A lattice defect (vacancy in our case) is surrounded by host lattice atoms which are displaced from their regular positions (fig. 5.2.2.18). As was shown in [119] Fe\(^{3+}\) ions move about 0.2Å towards the vacancy. Scattering on defects is therefore determined by the interference between contributions of the vacancy itself and the displacement field, where the latter is scattering from the difference between the deformed and undeformed lattice. If the defect is static, the scattering is elastic [120-122]. If we put an oxygen vacancy at the origin such that the moduli of \( R_i \) are the distances between the oxygen vacancy and the undisplaced iron or titanium position, then \( u_i \) is a displacement of Fe or Ti atoms. We assume that a given vacancy does not displace the next oxygen vacancy. The structure factor due to distortion around the oxygen vacancy is to a first order approximation

\[ S(Q)_{\text{dis}} = |1 + e^{DWF} iQu(\nu)|^2, \]

(5.2.2.3)

where \( q = Q - G \) is the distance of the scattering vector \( Q \) from a reciprocal lattice vector \( G \) and \( e^{DWF} \) denotes the Debye-Waller factor . One can observe that the effect of the Debye-Waller factor is to attenuate the peak intensities, in particular at high momentum transfer. At the same
time the scattering function increases its value depending on the displacement $u_i$ resulting in an increase of coherent scattering (fig. 5.2.2.17).

- Models of the local motion

The common tendency of the EISF to change with the Q value demonstrates a common geometry of the local motion independent of the resolution function and the instrument used.

At present, we restrict ourselves to correlations only between energetically equivalent oxygen sites, assuming that correlations to all other atoms can be neglected. Here we discuss the local motion between two equivalent sites and consider the possibility of oxygen vacancy rotation in the (0k0) plane within a circle of three or four dwells and rotation of the oxygen vacancy in the octahedral entity within one unit cell.

Let us assume that the oxygen vacancy can jump between two equivalent sites (fig. 5.2.2.19). Then the measured EISF can be fitted with eq. (1.5.4.15) (section 1.5.4. Diffusive scattering. Rotational diffusion) and the result of the fit is given at fig. 5.2.2.21.
5. RESULTS. DYNAMIC PROPERTIES

Applying this model for the oxygen rotation within the plane with three (fig. 5.2.2.20a), four (fig. 5.2.2.20b) and six (fig. 5.2.2.20c) equivalent sites one can calculate the elastic (EISF) and the quasielastic structure factors (eq. (1.5.4.19), section 1.5.4. Diffusive scattering. Rotational diffusion). Four site and six site models involve two and three Lorentzian functions, respectively (table 5.2.2.6)

<table>
<thead>
<tr>
<th>a) N=3</th>
<th>b) N=4</th>
<th>c) N=6</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="a" alt="Diagram" /></td>
<td><img src="b" alt="Diagram" /></td>
<td><img src="c" alt="Diagram" /></td>
</tr>
</tbody>
</table>

Fig. 5.2.2.20. Jump model among a) three sites b) four sites and c) six sites equally spaced on a circle with radius of half of the unit cell

<table>
<thead>
<tr>
<th>N=3</th>
<th>N=4</th>
<th>N=6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0(Q) = \frac{1}{3} \left[ 1 + 2 j_0(Qr\sqrt{3}) \right]$</td>
<td>$A'_0(Q) = \frac{1}{4} \left[ 1 + 2 j_0(Qr\sqrt{2}) + j_0(2Qr) \right]$</td>
<td>$A_0(Q) = \frac{1}{6} \left[ 1 + 2 j_0(Qr) + 2 j_0(Qr\sqrt{3}) + j_0(2Qr) \right]$</td>
</tr>
<tr>
<td>$A_1(Q) = \frac{2}{3} \left[ 1 - j_0(Qr\sqrt{3}) \right]$</td>
<td>$A'_1(Q) = \frac{1}{2} \left[ 1 - j_0(2Qr) \right]$</td>
<td>$A_1(Q) = \frac{1}{6} \left[ 2 + 2 j_0(Qr) - 2 j_0(Qr\sqrt{3}) - 2 j_0(2Qr) \right]$</td>
</tr>
<tr>
<td>$A_2(Q) = \frac{1}{4} \left[ 1 - 2 j_0(Qr\sqrt{2}) + j_0(2Qr) \right]$</td>
<td></td>
<td>$A_2(Q) = \frac{1}{6} \left[ 2 - 2 j_0(Qr) - 2 j_0(Qr\sqrt{3}) + 2 j_0(2Qr) \right]$</td>
</tr>
<tr>
<td>$A_3(Q) = \frac{1}{6} \left[ 1 - 2 j_0(Qr) + 2 j_0(Qr\sqrt{3}) - j_0(2Qr) \right]$</td>
<td></td>
<td>$A_3(Q) = \frac{1}{6} \left[ 1 - 2 j_0(Qr) + 2 j_0(Qr\sqrt{3}) - j_0(2Qr) \right]$</td>
</tr>
</tbody>
</table>

Table 5.2.2.6. Expressions of the elastic and quasielastic structure factors, corresponding to the rotation jump models between four and six sites.

The models described above have been calculated and compared with the measured EISF (fig. 5.2.2.21) for the measurements at 1000°C with two resolutions as an example.
Fig. 5.2.2.21. Elastic incoherent structure factors (1000°C) for measurements with 15µeV and 70µeV compared to the models presented in the text
   a) two sites    b) three sites    c) four sites    d) six sites

The best fit is observed for the two sites model with jump distance of 7.76±0.43Å for 1000°C. This distance corresponds to the double unit cell for SrTi$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (a=3.885 Å) within the error bars.

Careful analysis of the quasielastic structure factors (fig. 5.2.2.22) reveals consistently higher intensity for the high resolution data pointing to a dependence of the quasielastic structure factor on the initial wave length (eq. (5.2.2.1)). This indicates that there are more crystallographic sites involved in the local motion. However, the dominating resulting wave vector transfer remains the same 0.81Å$^{-1}$, corresponding to 7.7Å - double the distance of the unit cell.
5. RESULTS. DYNAMIC PROPERTIES

Based on the models and the assumptions developed above one can propose two types of local motions observed in the high and low resolution measurements. Following the well known mechanism, Ti on octahedral sites is replaced by Fe\(^{3+}\) forming oxygen vacancies to balance the charge. According to models proposed \[72, 75, 76\] the introduction of the first two Fe atoms results in the formation of two pentacoordinated sites and a monomer (a single oxygen vacancy). A dimer can be formed with the substitution of two more Fe atoms, forming a tetrahedral site plus two original pentacoordinated sites. A trimer can be formed with the substitution of two more Fe atoms, but there is a choice of position, forming either a linear or a kinked chain. Thus, the minimum number of vacancies per chain is one and a higher concentration of Fe increases the chain length.

According to Mössbauer spectroscopy, \(\text{SrTi}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}\) spectra shows a mixture of Fe\(^{3+}\)(VI), Fe\(^{3+}\)(V) and Fe\(^{3+}\)(IV). Data show that the structure has randomly distributed a small amount of monomers and a large amount of dimers or trimers; thus oxygen can jump either directly to the next unit cell or perform ‘detours’ combining four and two (or three and three) sites jumps resulting the same final momentum transfer (fig. 5.2.2.23). One can assume that local jumps exists within monomers as well, which can be also detected by very low resolution QENS experiments.

Fig. 5.2.2.22. Measured quasielastic structure factors at 1000°C-open violet symbols (10.5 Å), open blue symbols (5.5 Å) and 800°C-closed violet symbols (10.5 Å), closed blue symbols (5.5 Å). Incoming neutrons with a different \(\lambda_0\) do “see” different sites occupied by oxygen (higher intensity-more crystallographic sites involved)
On the basis of already calculated activation energies for those two motions one can extract the characteristic jump times and compare them with electrical conductivity data (fig. 5.2.2.24). The Arrhenius plot confirms our finding of the two types of local motions exhibiting fast direct jumps (5.5Å) and slow indirect jumps (10.5Å and 6.27Å). One should note a very good fit of the data measured at two different instruments IN5 (10.5Å) and IN16 (6.27Å) indicating the same manner (indirect jumps) of the local motion. Electrical conductivity data can not be directly compared to the QENS findings because in the first case the translational diffusion is measured which is much slower than rotational motion.

Fig. 5.2.2.23. A two local jumps type model. Oxygen can perform direct jumps from A to B (fast motion) or indirect jumps A-C-D-B or A-D-E-B or A-C-D-E-B (slow motion)

Fig. 5.2.2.24. Arrhenius plot of the characteristic jump times measured at different neutron spectrometers IN5 (10.5Å, 5.5Å), IN16(6.27Å) and by means of electrical conductivity.
Chapter 6

Summary

The influence of the oxygen defects in (Ca, Sr, Ba)(Ti,Fe)O$_{3-\delta}$ systems on the static and dynamic properties has been studied using various techniques which are sensitive to different length scales. The number of vacancies was varied by changing the amount of substituted Ti$^{4+}$ by Fe$^{3+}$. Due to the strong correlation with the crystal structure physical properties such as temperature, pressure or chemical composition change with the variation of parameters. Static properties in BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ samples synthesised over a range of compositions were studied by means of Mössbauer spectroscopy to investigate cation distribution and short-range ordering of oxygen vacancies, and to discuss potential implications for the interpretation of conductivity data. Detailed dynamic studies on microscopic (QENS) and macroscopic (electrical conductivity) lengths were performed on CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ and SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ systems. The samples were prepared via solid state reaction and then characterized by room temperature x-ray diffraction (phase purity, determination of the lattice parameters) and by electron microprobe analysis (homogeneity, off-stoichiometry). Additionally, neutron diffraction measurements were done on the SrTi$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ composition showing a magnetic transition from antiferromagnetic to paramagnetic state (Néel point) at ca. 200°C. The fact that Fe atoms carry a magnetic moment and create a magnetic superstructure does not complicate the data analysis of quasielastic data, but in that way additional information about the guest atoms could be obtained. The structural defects due to the deviation from stoichiometry are very important for the electrical transport because high conductivity can be often ascribed to a high concentration of point defects. With increase of oxygen vacancies (equivalent to an increase in iron content) there are two competing effects. Ionic conductivity initially will increase because the concentration of mobile species (vacancies) increases. On the other hand, larger and larger vacancy clusters form when the concentration of these defects increases, leading to a decrease in mobility and thus in electrical conductivity. Based on these considerations BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ with x=0.1-0.6 compositions were studied by means of Mössbauer spectroscopy. Mössbauer spectroscopy showed all iron to be present as Fe$^{3+}$, occurring in octahedral and pentahedral sites. Analysis of area ratios indicates that oxygen vacancies are distributed randomly over O1 sites, and that a random distribution of Fe and Ti cations over M1 and M2 sites is consistent with the data. No
6. SUMMARY

evidence for ordering of oxygen vacancies was found. Results are consistent with conductivity results which show generally increasing ionic conductivity with increasing oxygen vacancy concentration.

Electrical conductivity measurements allow access to the dynamical properties on a macroscopic scale. A set of measurements was obtained for CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ with $x=0.3$. The electrical conductivity was measured at $T=1000^\circ$C, 1100$^\circ$C, 1200$^\circ$C in the fugacity range from $10^{-6}$ to $10^{-14}$ atm. By means of electrical conductivity relaxation it was shown that ionic conductivity extracted from the observed relaxation times is independent of the fugacity setting, while the magnitude of the conductivity is given by the electronic transport properties. The ionic conductivity obtained in the traditional way from the minimum of the total conductivity at intermediate fugacity values corresponds to ionic conductivity derived from relaxation constants. A new method of ionic transport study is proposed.

Oxygen translational diffusion in SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system was studied by means of electrical conductivity and the atomistic local motions by QENS. Electrical conductivity was investigated in a broad range of the oxygen partial pressure and different temperatures. Qualitatively the dependencies of the conductivity contributions on $P_{O_2}$ are as predicted from the simple defect model presented, in which oxygen vacancies charge compensate iron substitution in titanium and with the presence of electron and hole defects. This gives an essentially ionic conductor with n- and p-type electronic contributions at, respectively, low and high oxygen partial pressures. A linear dependence of the activation energy over the measured temperature range and iron content shows no indication for the oxygen vacancies ordering transition. The activation energy of vacancy migration is calculated. The high level of mixed ionic/electronic conductivity makes such a system interesting for oxygen extraction and as components of electrodes for ceramic fuel cells and electrochemical reactors.

The quasielastic neutron scattering revealed two types of localized oxygen motion in SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ ($x=0.5$, $x=0.8$) with $Q$ independent behaviour of the FWHM of the quasielastic line. The experimental EISF has been analyzed through several models for the geometry of the rotations. An innovative model of the local oxygen motion was proposed involving oxygen jumps along the (0k0) plane either directly to the next unit cell or performing ‘detours’ combining four and two (or three and three) site jumps resulting in the same final momentum transfer. The activation energies of the rotational process of 0.43eV and 0.27eV have been obtained for the ‘fast’ and ‘slow’ jumps, respectively.
In any case the combination of long-range and short-range diffusion techniques is essential for a comprehensive understanding of the structure-diffusion relations, which in turn is a prerequisite to tailor functional materials with optimised properties.
Zusammenfassung

Der Einfluss von Sauerstoffdefekten auf die statischen und dynamischen Eigenschaften in (Ca, Sr, Ba)(Ti,Fe)O$_{3-\delta}$-Verbindungen wurde mit verschiedenen Methoden untersucht, die auf unterschiedlicher Längenskalen empfindlich sind. Die Anzahl der Leerstellen wurde variiert indem unterschiedliche Anteile von Ti$^{4+}$ durch Fe$^{3+}$ substituiert wurden. Die Kristallstruktur ist stark an die Variation von physikalischen Parametern wie Temperatur, Druck oder auch an die chemische Zusammensetzung gebunden. Die statischen Eigenschaften von BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ Proben unterschiedlicher Zusammensetzungen wurden mit Mößbauerspektroskopie untersucht mit dem Ziel, die Kationverteilung und Nahordnungen der Sauerstoffleerstellen zu bestimmen und um mögliche Auswirkungen auf die Interpretation der Leitfähigkeitsdaten diskutieren zu können. Detaillierte dynamische Untersuchungen auf mikroskopischer (QENS) und makroskopischer (elektrische Leitfähigkeit) Längenskala wurden an Proben aus CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ und SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ durchgeführt.

Die Proben wurden über Festkörperreaktionen synthetisiert und anschließend bei Raumtemperatur durch Röntgenbeugung (Phasenreinheit, Bestimmung des Gitterparameters) und Elektronenmikroskopie (Homogenität, Stöchiometrieabweichung) charakterisiert. Zusätzlich wurde mittels Neutronenbeugung die Verbindung SrTi$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ untersucht, die eine magnetische Phasenumwandlung von antiferromagnetisch nach paramagnetisch bei etwa 200°C zeigte (Néel Temperatur). Die Datenanalyse der quasielastischen Spektren wird durch die Tatsache, dass das Fe-Atom ein magnetisches Moment trägt und eine magnetische Superstruktur ausgebildet, nicht erschwert. Allerdings erlaubt dieses Faktum zusätzliche Information über das Gastatom zu erkennen.

Strukturelle Defekte auf Grund einer Abweichung von einer stöchiometrischen Verbindung sind für den elektrischen Transport von großer Bedeutung, da eine hohe Leitfähigkeit oft einer hohen Konzentration von Punktdenekten zugeordnet werden kann. Zwei konkurrierende Effekte treten bei einer zunehmenden Anzahl von Sauerstoffdefekten auf (äquivalent mit einem zunehmendem Eisengehalt). Anfangs wird die ionische Leitfähigkeit zunehmen, da sich die Konzentration der mobilen Spezies (Leerstellen) erhöht. Andererseits bilden sich immer größere Leerstellenclusters wenn die Konzentration dieser Defekte ansteigt. Dies verringert die Beweglichkeit und damit auch die elektrische Leitfähigkeit. Auf diesen Vorstellung aufbauend wurden BaTi$_{1-x}$Fe$_x$O$_{3-x/2}$ Proben mit $x=0.1-0.6$ mit Mößbauerspektroskopie untersucht. Mößbauerspektroskopie zeigte, dass Eisen in Form von Fe$^{3+}$
Summary


Messungen der elektrischen Leitfähigkeit geben Zugang zu den dynamischen Eigenschaften auf einer makroskopischen Längenskala. Ein Datensatz wurde für die Verbindung CaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ mit $x=0.3$ aufgenommen. Die elektrische Leitfähigkeit wurde bei $T=1000^\circ$C, $1100^\circ$C, $1200^\circ$C und bei Fugazitäten von $10^{-6}$ to $10^{-14}$ atm bestimmt. Eine Analyse des Relaxationsverhaltens der elektrischen Leitfähigkeit zeigte, dass die ionische Leitfähigkeit, die aus der Relaxationszeit abgeleitet werden kann, unabhängig von der Fugazität ist, während der Wert der Leitfähigkeit durch die elektronischen Transporteigenschaften bestimmt ist. Die ionische Leitfähigkeit, die in traditioneller Weise aus dem Minimum der Gesamtleitfähigkeit bei mittleren Fugazitätswerten bestimmt ist, stimmt mit der Leitfähigkeit aus dem Relaxationsverhalten überein. Darauf aufbauend wird eine neue Methode zur Bestimmung des ionischen Transports vorgeschlagen.


Quasielastische Neutronenstreuung an SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ ($x=0.5$, $x=0.8$) zeigte zwei Arten von lokalisierter Sauerstoffbewegung, wobei die FWHM der quasielastischen Linie unabhängig von $Q$ sind. Der experimentelle EISF wurde mit mehreren Modellen für die
Geometrie der Rotationsbewegungen verglichen. Ein neuartiges Modell wird für die lokale Sauerstoffbewegung vorgeschlagen mit Sauerstoffsprüngen in der (0k0) Ebene, die entweder direkt in die nächste Einheitszelle führen oder einen „Umweg“ beinhalten, der vier und zwei (oder drei und drei) Platzwechsel involviert, die in ihrer Summe den gleichen Impulsübertrag ergeben. Die Aktivierungsentnergien der Rotationsbewegungen betragen 0.43eV und 0.27eV für die „schnellen“ und „langsamen“ Sprünge.

Die Zusammenschau von langreichweitigen und kurzreichweitigen Methoden zur Diffusionsbestimmung erweist sich als wesentlich, um die Beziehungen zwischen Strukturen und Diffusion umfassend zu verstehen. Andererseits ist dies eine wesentlich Voraussetzung um funktionelle Materialien mit optimierten Eigenschaften zu herzustellen.
Chapter 7

Outlook

Also the investigations presented have been successful in identifying microscopic diffusion modes; a unique interpretation of diffusion geometry on an atomic scale has remained limited because of the use of polycrystalline samples. A major advance for the determination of the diffusive path can be expected if single crystals of sufficient size were available. Single crystals are difficult to produce and to obtain the desired composition x.

A single crystal conductivity study could help to avoid grain boundary conduction and precise measurements of metal-oxygen distances with neutron diffraction can be used to determine the valence state of the metal ions. The accurate measurement of metal-oxygen distances in oxides can help in the understanding of the crystal chemistry, and in the search for new materials.

Single crystal elastic scattering can be used to obtain structural details that may be missed with powder diffraction, since single crystals allow an exploration of 3D scattering space, while powder diffraction reduces to one dimension – intensity versus d-spacing. Single crystal inelastic neutron scattering can be used to investigate the dynamics of the structure, and also the magnetic properties of the atoms. The anisotropy of diffusion properties can be followed by quasi elastic scattering.

The SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ system exhibits a magnetic ordering which depends on the iron content. Up to now there is no research on the magnetic properties of this system and no investigation of whether partial displacement of the Ti$^{4+}$ by Fe$^{3+}$ induces superexchange interactions. Magnetic properties of strontium ferrite had been studied using Mössbauer spectroscopy and magnetic susceptibility. The single crystals would allow precise studies of their magnetic structures using single crystal neutron experiments.

The phase diagram of SrTiO$_3$-SrFeO$_{2.5}$ is not well established. For the material applications it is very important to determine a possible order-disorder transition in the oxygen sublattice as a function of temperature and oxygen partial pressure.

Studies on (Ca, Sr, Ba)Ti$_{1-x}$Fe$_x$O$_{3-\delta}$ systems show that Fe-substitution leads to a considerable rise in conductivity. It would be interesting to investigate the ionic conduction in the perovskite-type oxides doped with other cations of valence lower than Ti.
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**Curriculum vitae**

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